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NITRATE REMOVAL
FROM
WASTEWATERS
BY
ION EXCHANGE

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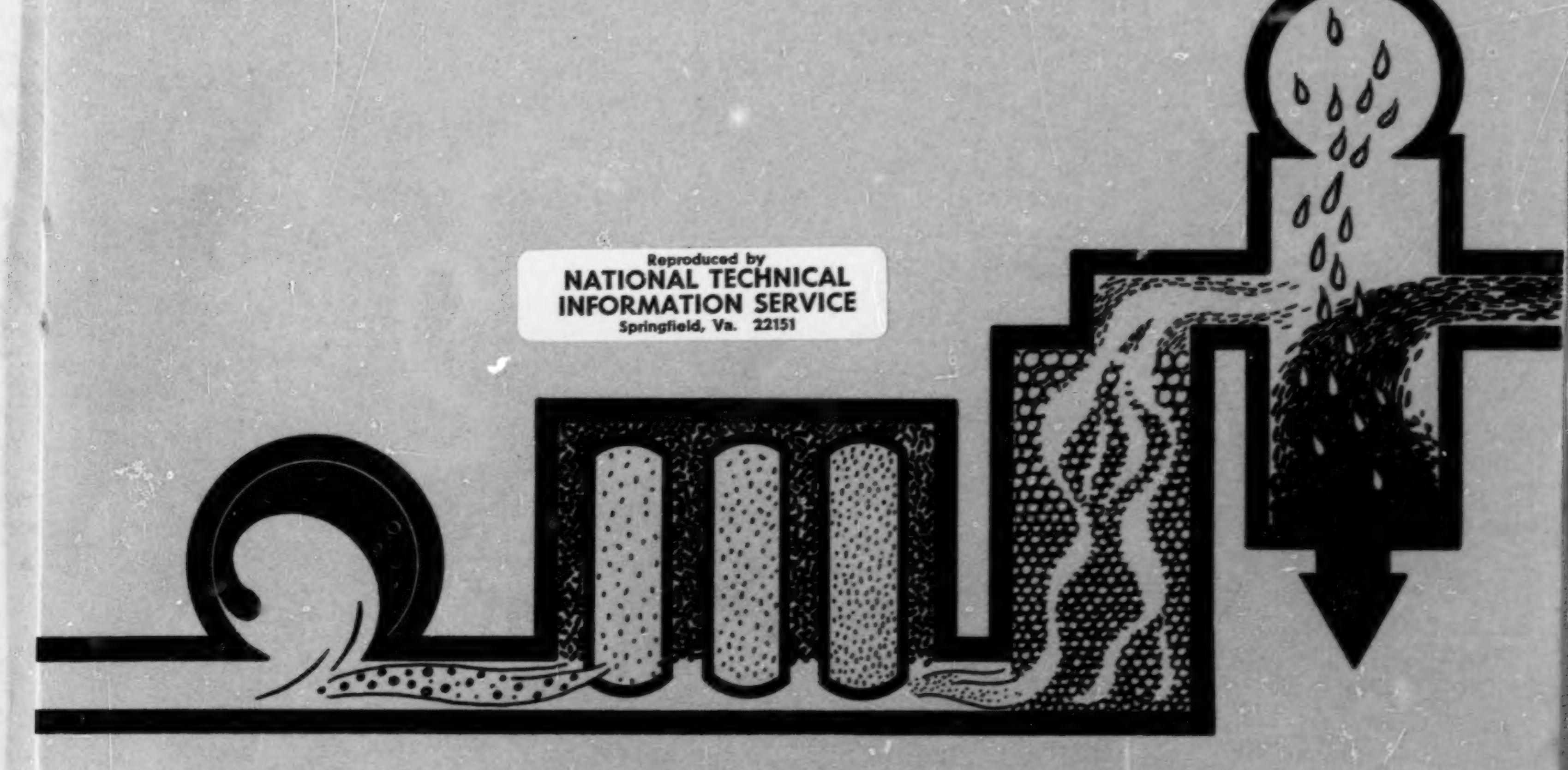

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16. Abstract

Alkylated amidines dissolved in an aromatic hydrocarbon were absorbed in macro-porous polystyrene beads to form a water-immiscible extractant system for the removal of nitrate from wastewaters. The amidines are relatively strong bases and possess the advantage over the simple aliphatic amines that they exist in the salt form in contact with wastewaters in the pH range of 7.0 to 8.0. They can, however, be readily regenerated with alkalis, such as ammonia or sodium hydroxide. Amidinium ion in the organic phase selectively extracts nitrate ion over chloride ion by a factor of about 20 (nitrate/chloride ratio in the organic phase is about 20 times the ratio in the equilibrium aqueous phase), and nitrate over sulfate and bicarbonate by much higher ratios. Therefore, amidine systems will pick up mainly nitrate ion from municipal wastes. 70 bed volumes of a synthetic municipal wastewater containing 62 ppm nitrate ion and 350 ppm chloride ion were treated before breakthrough of nitrate ion in the effluent. Processing costs were estimated currently at 16¢/1000 gal. (Lowry-~~Tex.~~ Texas)

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NITRATE REMOVAL FROM WASTEWATERS BY ION EXCHANGE

by

The Dow Chemical Company
Walnut Creek, California 94598

for the

WATER QUALITY OFFICE

ENVIRONMENTAL PROTECTION AGENCY

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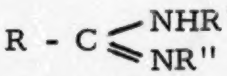
ABSTRACT

This report describes an exploratory experimental study of the use of porous polymer beads containing a water-immiscible extractant system for the removal of nitrate from waste waters.

Alkylated amidines,  $R - C\begin{array}{l} \diagup NHR' \\ \diagdown\!\!\!\diagdown NR'' \end{array}$ (R's are octyl through dodecyl), proved to be a suitable class of compounds for the extractant system. The amidines are relatively strong bases, and possess the advantage over the simple aliphatic amines that they exist in the salt form in contact with waste waters in the pH range of 7-8. They can, however, be readily regenerated with alkalis, such as ammonia or sodium hydroxide.

The amidinium ion in the organic phase selectively extracts nitrate ion over chloride ion by a factor of about 20 (i.e., the nitrate/chloride ratio in the organic phase is about 20 times the ratio in the equilibrium aqueous phase), and nitrate over sulfate and bicarbonate by much higher ratios. From typical municipal waste waters amidine systems will therefore pick up mainly the nitrate ion.

Amidines dissolved in an aromatic hydrocarbon were absorbed in macroporous polystyrene beads and used to treat a synthetic municipal waste water containing 62 ppm nitrate ion and 350 ppm chloride ion. Beds of this material treated up to 70 bed volumes of water prior to breakthrough of the nitrate in the effluent. The absorbed nitrate ion was removed with either ammonia or sodium hydroxide. Soluble losses of the extractant were in the range of 1-20 ppm, and could be reduced to well below 1 ppm by proper choice of materials.

This report was submitted in fulfillment of Project Number 17010 FSJ, Contract 14-12-808, under the sponsorship of the Water Quality Office, Environmental Protection Agency.

Key Words

Nitrates
Denitrification
Waste Water Treatment
Municipal Wastes
Water Pollution Treatment
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CONCLUSIONS AND RECOMMENDATIONS

The major accomplishment of this project has been the elucidation of the chemistry of high molecular weight amidine as liquid-liquid extraction agents. The chemistry exhibited by these materials identifies them as both unique and adequate materials for the removal of nitrate from waste waters. They exhibit sufficient basicity to form salts in contact with neutral aqueous solutions. They are, on the other hand, sufficiently weak in base strength to be converted back to the base form with either ammonia or alkali. They exhibit good selectivity for nitrate ion over other common inorganic anions. Soluble losses of the salt form to dilute aqueous solutions can be kept in the region of one ppm or less. And finally, they are quite stable toward hydrolysis by alkali, when used in hydrocarbon diluents. Soluble losses of the amidines and the aromatic hydrocarbon diluent used in this study were not as low as desirable for optimum economic performance. However, on the basis of the studies, it is clear that minor modifications would probably eliminate this factor as an economic problem.

Absorption of hydrocarbon solutions of amidines into porous polymer beads provides a means of utilizing the chemistry of the amidines to remove nitrate from water. Column experiments have demonstrated that removal of nitrate can be effectively accomplished at low concentrations and in the presence of typical chloride concentrations. The major drawback of the extractant-in-bead approach is the relatively low (compared to conventional ion exchange) total exchange capacity of the beads. This factor results in low feed water capacity per cycle, and in low nitrate concentration in the eluate. The former leads to an increase in resin bed requirement, while the latter increases the volume of eluate to be discarded or evaporated for discard.

Further improvement of the extractant-in-bead system can probably be expected by further study of the processing variables. Use of two beds in series, or the recycling of some of the lower concentration portions of the eluate, or use of slower elution flow rates, may all lead to higher eluate concentrations and lower evaporation costs. In some situations direct utilization of the eluate as a fertilizer material might eliminate the evaporation requirement altogether.

A rough projection of processing costs, based on the data of this study and an earlier cost estimate for ion exchange processing of waste water for nitrate removal, indicate a cost in the range of 16¢ per thousand gallons (16¢/M gal) of feed. Of this, about 10 ¢ is required for evaporation of the eluate to a 40% sodium nitrate-sodium chloride solution. Further development may determine that this evaporation requirement can be lowered, but it probably cannot be eliminated. The ultimate processing cost can probably be expected, therefore, to fall in the range of 5-10¢/M gal.

Amidine compounds can probably be utilized in other ways than absorption in polymer beads. The simplest competitive method would be conventional liquid-liquid extraction.

On the basis of these conclusions, we recommend the following:

1. Development of this system should be continued to a limited extent, in order to obtain a clearer picture of the nature of the elution process. The work should be concentrated on the effects of the operating variables such as flow rate, bed depth, bead size and type, and eluant type and strength. The importance of estimating the final eluate concentration lies in the dominant position of the evaporation cost required to reduce its volume for disposal or transport for use. A secondary question, which should receive some effort, is whether diluent-free beads (containing extractant only) will be effective, since greater concentrations of extractant may then be achievable.

2. Other potential means of utilizing the amidines for nitrate removal should be considered. Conventional liquid-liquid extraction is a significant possibility. This, and any other promising ideas for utilizing the amidine chemistry in other contacting systems should be explored in a preliminary way and compared to the use of polymer beads prior to any further development of the latter beyond that described in recommendation 1.

INTRODUCTION[1]

Nitrogen Compounds in the Environment

Nitrogen compounds are fundamental components of all biological systems. They are not only required for maintenance of these systems, but are also found as waste products from the metabolism of biological systems, and are released to the environment in the decomposition of these systems after death. Because of this strong role played by nitrogen, the functioning of biological systems and the maintenance of delicately balanced relationships among them is often critically dependent upon the nature and levels of nitrogen compounds existing in the environment.

Until recent years man's major concern with nitrogen was with the use of nitrogenous fertilizers to increase the yield of crops. The quantity of nitrogen compounds in waste streams from his activities has heretofore been sufficiently small that any effects on the environment have gone unnoticed. Within the last several years, however, the increasing concentrations and quantities of both plant nutrients, phosphorus and nitrogen, in water bodies have led to the recognition of a number of environmental problems. Studies have identified the major sources of these compounds, which, in the case of nitrogen, are agricultural runoff and municipal and industrial waste water discharges(3). Minor amounts are contributed by urban runoff and rainwater.

One major problem is the occurrence of nitrate compounds in ground water. Nitrate ion can appear here either from use of nitrates as fertilizers, or from the oxidation of other nitrogen compounds in the soil by bacteria. Nitrates are quite soluble in water and are not readily adsorbed on soil particles, and the percolation of rain or irrigation water through the soil readily carries nitrates into the ground water table . This situation has created a public health problem in some areas, since nitrate is responsible for the condition known as methemoglobinemia in very young infants (4). Nitrate is also toxic to adults, though at considerably higher levels, and the U.S. Public Health Service has set a limit of 45 ppm of nitrate for drinking waters(5).

---

[1] This introduction is intended to provide only a brief summary of the nitrate problem. For a more detailed examination of the problem, the reader should consult the proceedings of the Conference on Nitrate and Water Supply, held in 1970 (1). A bibliography of material on the sources and effects of nitrate is also available (2).

Significant concentrations of nitrate in ground water have been reported in various locations in California (4, 6) in several midwestern and eastern states (7, 8, 9) and abroad in Israel and Germany (10) (11). Many of these contain nitrate at greater than 50 ppm and represent, therefore, potential hazards not only to humans, but also to livestock which may be required to use them.

A second major problem associated with the existance of nitrates in water is the occurrence of algae blooms or explosive growths of algae. The latter, being plants, require nitrogen and phosphorus as nutrients, and utilize carbon dioxide in their metabolism. Under certain conditions algae blooms occur in natural water systems, after which the decomposition of the dead algae by bacteria consumes oxygen and often results in extensive fish kills. Increasing frequency of blooms, and their close association with sewage discharges has implicated both nitrogen and phosphorus as contributors. High levels of carbon dioxide have also been suggested as the crucial factor (12). At this point the relative importance of these factors, as well as others, has not been clearly established. It seems clear, however, that increasing sewage loading of natural water bodies by increasingly populous urban areas will probably require more extensive treatment of sewage, probably including major reduction of total nitrogen concentration.

Nitrogen occurs in sewage mainly as organic nitrogen or ammonia, and passage through most secondary sewage plants, while decomposing the organic material, still leaves the nitrogen mainly in the ammonia form (13). Modifications in plant operation can, however, convert most of the nitrogen to nitrate, if desired (14, 15, 16).

An additional source of nitrogen compounds in the environment is agricultural drainage obtained from underground tile drain systems. In California extensive drainage systems are used in the Central Valley and volumes of up to 500,000 acre feet of water containing up to 100 ppm of nitrate are anticipated during the next 50 years (17). A considerable controversy surrounds proposals to discharge this waste stream into the Sacramento-San Joaquin river delta, and considerable interest currently exists in possible means for eliminating nitrate from this water stream.

Removal of Nitrates from Water

Because of the emergence of the nitrogen problem considerable research effort has been devoted to methods for eliminating ammonia and nitrates from water (1, 18). The major methods in existence or under study include bacterial reduction of nitrate to nitrogen (denitrification), utilization of nitrate by algae, air stripping of ammonia, and selective ion exchange removal of ammonium ion. These methods are summarized in several surveys of the problem (1, 18, 19).

At this time the most promising method for nitrate removal appears to be the anaerobic denitrification process. It has been known for some time that under anaerobic conditions, in the presence of organic matter, certain bacteria will reduce nitrate to nitrogen gas. The process has been actively studied as a means of eliminating nitrates from water (3, 18, 20). For removing nitrogen compounds from sewage, an additional nitrification step beyond the normal secondary treatment is required. In this step, a bacterial culture is maintained to oxidize ammonium compounds to nitrates. The effluent from this step is fortified with a suitable organic substrate, usually methanol, and is conducted through an anaerobic pond or tank containing a culture of denitrifying bacteria. For waste waters containing nitrate in the range of 20 mg N/l a 90% removal is readily achieved with costs in the range of 8 ¢/M gal (1). The process has been operated on scales as large as 1 mgd and a 300 mgd plant is being planned in Washington, D.C. (18). The process has also been tested on subsurface agricultural drainage at the Firebaugh test station in California, apparently also with success (20).

Nitrate can also be removed from water with conventional anion exchange resins (1, 21, 22, 23). Most commercial materials exhibit a selectivity for nitrate over chloride of 2 or 3*, with the result that a water containing nitrate to chloride ratio of, say, 0.1, will result in a loaded resin containing a ratio of 0.2 or 0.3. The difficulty arises in the fact that the absorbed nitrate is relatively difficult to remove with the standard sodium chloride regenerant, and the problem of disposing of the regenerant solution containing the nitrate still remains. A cost estimate for such a process, including an additional liquid-liquid extraction step to concentrate the nitrate into an ammonium nitrate product, was prepared in this laboratory under a recent contract (24). The total treatment cost, which applied to that treatment of agricultural drainage water, was found to be about 16¢/M gal from which a credit of about 3¢ could be anticipated for the value of the ammonium nitrate.

---

* Selectivity is defined as the nitrate/chloride ratio in the resin phase divided by the ratio in the solution phase. It can also be defined as the ratio of distribution coefficients (resin/solution) of nitrate over chloride.

This estimate was based on a fairly large plant (100 mgd), but also was based on a rather unfavorable water conposition (about 7,000 ppm total dissolved solids). Application to a sewage stream, where less dissolved solids are usually found, might be a more attractive proposition.

A specific task of that contract was also to estimate the effect of using resins of higher selectivity for nitrate over chloride. Using a selectivity value of 20, the corresponding treatment cost for the same waste stream was about 6 ¢/M gal, from which, again, a credit of about 3¢ could be anticipated for the ammonium nitrate product.

With this information, the goal of the work reported here has been to develop a material with a considerably higher nitrate/chloride selectivity than is available in existing exchange resins. The approach has been in the direction, not of a conventional exchange resin, but of a porous resin bead containing a water-immiscible liquid ion-exchanger.

Basis of the Extractant-in-Bead Approach

The problem of development of more selective resin materials can be broken into two parts: the search for a phenomenon which can provide the desired selectivity under any conditions at all; and the adaptation of this phenomenon to a resin system. Certain aliphatic amine solvent extraction systems are known to exhibit fairly high selectivity for nitrate over chloride and other common ions (25), and selective extraction of nitrate from mixtures of anions based on this phenomenon is easily conceivable.

Solvent extraction systems, however, while quite useful for processing various industrial materials, are less attractive for processing water. This is partly a matter of economics, since water, at, say, 50¢/M gal., is many times less valuable than most industrial process solutions. However, in processing water, an additional consideration arises, namely, that of providing an effluent containing a minimum of organic matter which could contribute to a subsequent pollution problem.

A major source of organic material from a liquid-liquid contact is the physically entrained solvent system, left after coalescence of the bulk of the extractant phase. One possible means of circumventing this problem is to use a solid absorbent in which is contained the desired liquid extractant system, eliminating the need to disperse the organic liquid to obtain liquid-liquid contact.

Solid Absorbent Materials. The use of liquids adsorbed on porous solid materials forms the basis of reversed phase partition chromatography. The first published use of a gel type polymer bead seems to have been that of Small (26, 27, 28), who used cross-linked polystyrene beads to absorb tributyl phosphate solutions in organic diluents. These materials were found to be fairly effective for extracting uranium from aqueous solutions, by analogy with the liquid-liquid systems which have been used for the same purpose.

A patent has been granted for a similar process covering the use of solid adsorbents containing aliphatic amines or esters of phosphoric acid for removing metal ions from aqueous solution (29). A related patent described the use of activated charcoal containing ethanolamine as an absorbent for gaseous carbon dioxide (30).

Small used the gel type beads, which consist of a more or less uniform polymeric matrix, with occasional cross-links to render the material insoluble. In principle, however, any hydrophobic material, including activated carbon, could be used, which would absorb the water-immiscible solvent system preferentially over water.

We considered the use of activated carbon, but an examination of the major types currently available revealed that most materials possessed much smaller pore sizes than we believed desirable. The use of the gel type polystyrene beads appeared unattractive since the diluent system must be one which swells the polystyrene matrix. We therefore confined our attention to the so-called "macroporous" or "macroreticular" beads, which consist of a network of cross-linked polymer structures, but contain also relatively large pores or voids, with diameters up to several hundred Angstroms(31). The rationale behind these materials was that such pores were small enough that the organic phase would resist hydraulic or mechanical forces which might tend to strip away the organic liquid. They would on the other hand, be large enough to allow essentially bulk solution behavior; i.e., diffusion of dissolved materials would be about as rapid as in a bulk liquid. This is of considerable practical importance, since one of the characteristics of gel type ion exchange resins is that dissolved species exhibit much lower diffusion coefficients in the resin phase than in the solution outside.

Extractant Systems. While the polymer beads were available as materials at the start of this study, none of the extractant systems existed. Four major requirements must be satisfied by an extractant, to be considered useful in this application. They are as follows:

1. It must be susceptible to being stripped or eluted of anions with alkali;
2. It must exhibit suitable ion selectivity alone or in an appropriate diluent;
3. It must be sufficiently basic to remain in the salt or cationic form at the pH of natural waters (presumably in the range 7-8);
4. It must be sufficiently hydrophobic to be strongly retained by the bead, and exhibit only very small soluble losses to the aqueous stream treated.

The first requirement is relatively easily satisfied by using a non-quaternary amine (i.e., tertiary, secondary, or primary) wherein the presence of the proton in the substituted ammonium ion provides pH sensitivity. Reaction of the amine salt with a base converts the salt to a neutral molecule and results in removal of the inorganic anion from the organic phase as follows:

$$\overline{R_3NH^+ \; NO_3^-} + Na^+ + OH^- \longrightarrow \overline{R_3N} + H_2O + Na^+ + NO_3^- \qquad (1)$$

(Barred species denote those in the non-aqueous phase.)

Adequate selectivity for nitrate also can be observed in the simple aliphatic amine systems. We define the selectivity constant as the equilibrium constant for the exchange reaction:

$$NO_3^- + \overline{R^+ \; X^-} \leftrightarrows \overline{R^+NO_3^-} + X^- \qquad (2)$$

$$S^{NO_3}_{X} = \frac{\overline{(NO_3^-)} \; (X^-)}{(NO_3^-) \; \overline{(X^-)}} \qquad (3)$$

This constant can also be thought of as the ratio of distribution coefficient of nitrate to the coefficient of some other ion, X^-. It is also equal to the nitrate/chloride ratio in the extractant divided by the nitrate/chloride ratio in the aqueous solution.

Earlier work with amine extraction systems had indicated (32) that primary amine systems were not particularly selective for nitrate over chloride, but that secondary, tertiary, and quaternary ammonium ion systems were selective, exhibiting constants of the order of 20 in favor of nitrate. Studies of other ions were considerably less detailed, but indicated that selectivity constants for nitrate over sulfate and bicarbonate were in the range of 100-500 (33).
In the case of sulfate, the constant S is the equilibrium constant for the reaction:

$$2NO_3^- + \overline{(B_2H_2SO_4)} \rightleftharpoons 2\overline{(BHNO_3)} + SO_4^= \qquad (4)$$

With respect to the basicity of the aliphatic amines, the situation is less satisfactory. This subject has also been investigated rather extensively by us (34), and a full discussion is beyond the scope of this report. It will be useful, however, to outline the situation in order to provide the basis of this application. Although we are considering a system in which the amine would be held in a bead, the treatment is essentially identical to the case of the amine in a liquid solvent system.

If we denote the free amine base by B, and the extracting anion by X^-, then in the equation

$$\overline{(BHX)} \rightleftharpoons \overline{B} + H^+ + X^- \qquad (5)$$

the dissociation constant is given by:

$$K_a = \frac{\overline{(B)}\ (H^+)\ (X^-)}{\overline{(BHX)}} \qquad (6)$$

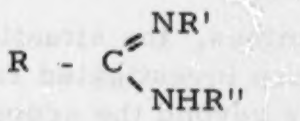
In order for the amine systems to function as liquid phase ion exchangers, it is necessary to operate in a pH range where the amine is primarily in the salt or ammonium form.

If we then wish to maintain 90% of the extractant in the salt form, and if we assume treatment of a waste water containing 0.01M chloride (about 350 ppm) and a pH of 7, we find that

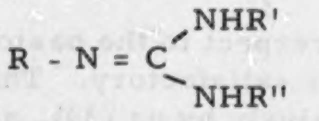
$$K_a = \frac{10^{-7} \times 0.01}{9} \approx 10^{-10} \qquad (7)$$

Thus, potential extractants must exhibit proton dissociation constants of 10^{-10} or less (pK_a of 10 or more) in order to be suitable for use in this problem. Although the lower aliphatic amine salts do exhibit pK_a values of this order of magnitude in water solution, the higher molecular weight homologs behave somewhat differently, and no pK_a values above about 8 or 9 have been reported (25, 34). Primary amines function as the strongest bases in liquid-liquid systems, but, as mentioned above, do not exhibit much selectivity.

At the time of writing of the original proposal on this subject, we suggested that the requirement of stronger basicity should be met by compounds of the amidine and guanidine types. The following are typical examples.



amidines



guanidines

Both types of compounds are known to be considerably stronger bases than aliphatic amines. This is clearly shown by the aqueous pK_a values (where K_a is the acid dissociation constant of the amine salt) of some typical representatives of these three types of compounds (35), which are given in Table I.

Table I

pK_a Values of Typical Organic Bases

Compound	**pK_a**
Ethylamine	**10.63**
Diethylamine	**10.93**
Triethylamine	**10.87**
Acetamidine	**12.40**
Benzamidine	**11.6**
Guanidine	**13.6**

Although, as mentioned above, the pK_a values are not directly usable in estimating behavior in liquid-liquid extraction systems, it is clear that amidines are at least 10 times as strong bases as the aliphatic amines, while guanidines are even stronger bases.

The synthesis portion of this study has accordingly been directed at these two classes of compounds, with primary attention given to the amidines.

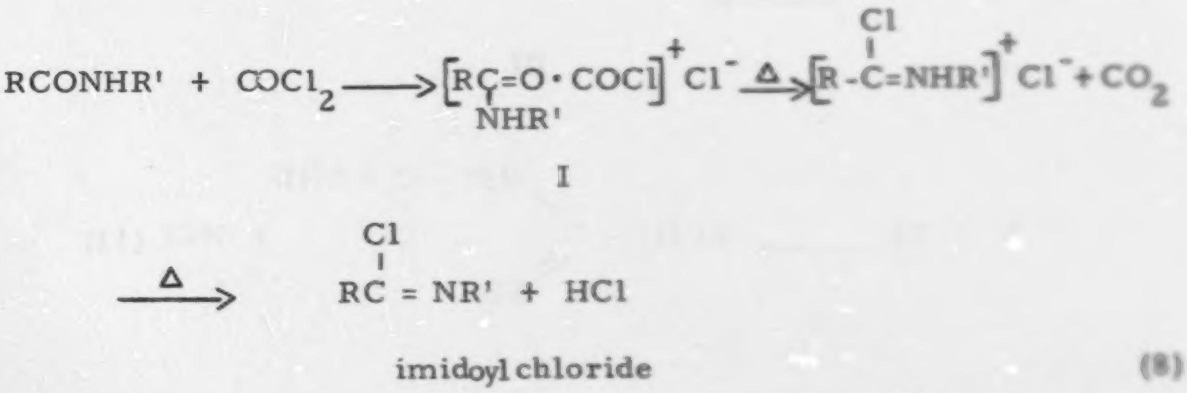
SYNTHESIS OF AMIDINES AND GUANIDINES

Amidines

Amidines can be considered as the nitrogen analogs of carboxylic acids, where the oxygen atoms of the latter have been replaced with nitrogen atoms plus the required number of protons. Amidines can be prepared in a number of ways, but all involve starting from some derivative of the corresponding carboxylic acid. Some general reviews of amidine chemistry, including their synthesis, have been published (36, 37).

In approaching the problem of amidine synthesis for this study, our major goal was to obtain sufficient material for small scale studies by procedures which could be conveniently carried out in the laboratory. However, we also wished to keep in mind the possibility that, should the process under study prove to be a practical one, the amidines should be capable of synthesis on a commercial scale by methods which would be reasonably economical and flexible. We selected, on this basis, the route involving halogenation of carboxamides to imidoyl halides, followed by reaction of this intermediate with an amine.

If an amide is allowed to react with any one of several inorganic acid chlorides, the following reaction occurs:



$$RCONHR' + COCl_2 \longrightarrow \left[\underset{NHR'}{RC}{=}O\cdot COCl\right]^+ Cl^- \xrightarrow{\Delta} \left[R-\overset{Cl}{\overset{|}{C}}{=}NHR'\right]^+ Cl^- + CO_2$$

I

$$\xrightarrow{\Delta} R\overset{Cl}{\overset{|}{C}} = NR' + HCl$$

imidoyl chloride (8)

The adduct, I, is metastable in most cases, and decomposes readily in this case to carbon dioxide and the iminium chloride, which in turn decomposes to HCl and the imidoyl chloride. Thionyl chloride, phosphorus pentachloride, phosphorus oxychloride and several other halides have been used to effect this reaction (38, 39, 40).

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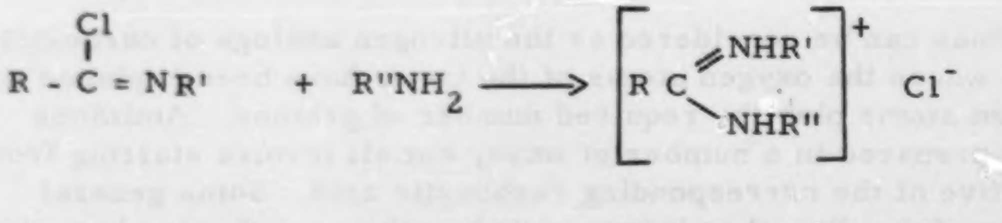
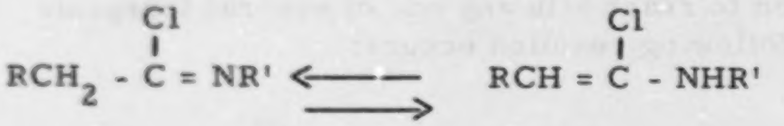
The imidoyl halide is a very reactive species, and reacts readily with nucleophilic species, much as the analogous acyl halides do. In the synthesis of amidines the reactant is an amine, giving the reaction



(9)

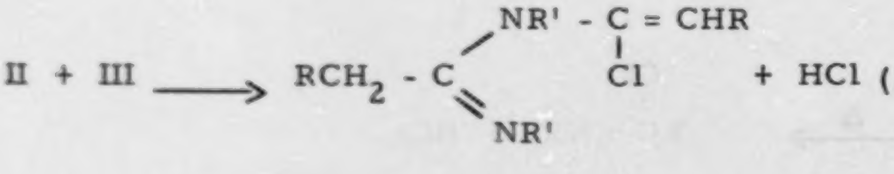
Both reactions apparently proceed readily, and yields of over 90% have been reported for both steps (40, 41, 42). Yields actually reported by various workers differ widely, and probably depend on the specific compounds under study, but the general procedure seems capable of producing relatively high yields of the desired products. We did not attempt to optimize our procedures but nevertheless were able to obtain yields in the 50-70% range.

The major source of difficulty appears to be a side reaction which occurs at the imidoyl halide stage (38). When the alpha carbon of the carboxyl group contains a proton, tautomerization of the imidoyl halide can occur, the tautomer then reacting with more imidoyl halide as follows:



$$RCH_2-\overset{Cl}{\overset{|}{C}}=NR' \rightleftharpoons RCH=\overset{Cl}{\overset{|}{C}}-NHR' \qquad (10)$$

II III



(11)

IV

The compound IV is still an imidoyl chloride, and can react with the amine in the final step of the reaction, thereby reducing the yield. Many workers in this field have, therefore, used formic acid derivatives (43), which have no alpha carbon, or aromatic acids (40) which have no alpha hydrogen. There is some evidence that sterically hindering the alpha carbon atom reduces the extent of this side reaction (38), and most compounds synthesized in this study used 2-ethylhexoic acid as the starting carboxylic acid, mainly for this reason.

The amides used as starting materials for the preparation of imidoyl halides were prepared in the conventional manner, using the acyl chloride and the appropriate amine in two fold excess. The reaction is

$$RCOCl + 2\,R'NH_2 \xrightarrow{\text{ether}} RCONHR' + R'NH_3Cl \qquad (12)$$

The amine hydrochloride was extracted from the ether with aqueous hydrochloric acid, and the amide was obtained by evaporating the ether.

Starting Materials

In most cases, starting materials were purchased from regular supply houses. In a few cases, we used commercial materials which consisted of mixtures, or were identified with trade names. The neodecanamide derivative was prepared from neodecanoyl chloride, purchased from both K & K labs, and from the White Chemical Company. The prefix "neo" is used to denote the absence of alpha hydrogens, but indicates nothing else about the structure of the hydrocarbon chain. Proton magnetic resonance patterns of the two samples indicated them to be quite similar, possibly identical, and confirmed the absence of alpha protons.

A second material used in these preparations was Primene 81-R[2], a primary aliphatic amine obtained from the Rohm & Haas Company. This is a mixture of isomers obtained by placing a primary amino group on a tertiary carbon of a branched chain hydrocarbon. This particular material exhibits an equivalent weight corresponding to an average of about 13 carbon atoms.

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[2] Mention of commercial products throughout this report does not imply endorsement by the Federal Water Quality Administration.

Products

The amines prepared in this program are listed in Table II. Detailed synthesis procedures are listed in Appendix I.

The amides, which were colorless, slightly viscous liquids, were characterized by elemental analysis and examination of their infrared spectrum. The products were of fairly high quality and were not further purified, but used directly in the next step. Some of the amides listed in the table were prepared in anticipation of their use in certain preparations which, because of lack of time, were not pursued.

The imidoyl halides were prepared in solution, but were not isolated. The amide and phosgene were mixed in toluene and allowed to stand overnight to form the imidoyl halide, according to equation 8. Excess phosgene was removed along with some diluent, under vacuum, in order to eliminate reaction with the final amine. Finally, the desired amine was added to the imidoyl halide solution and allowed to react, according to equation 9, to form the amidine salt.

Excess amine was removed by contacting the toluene with hot aqueous hydrochloric acid and then hot water. If the toluene were removed from the mixture at this stage, the product usually had a very high equivalent weight, 600 or more, instead of the desired value, which was usually in the range of 400.

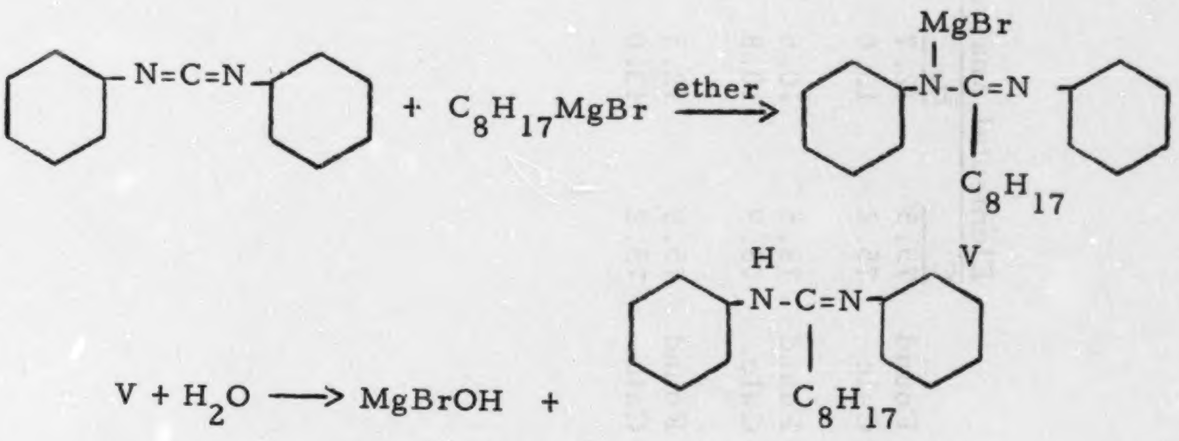
We found that the neutral impurity could be rejected rather well by partitioning the crude product between hexane or pentane and an ethanol-water medium. This system forms two phases as long as the water content of the ethanol remains above about 20%, and the ethanol remains almost entirely in the aqueous phase. In this system, the amidine hydrochloride enters the aqueous ethanol phase, leaving the neutral impurity in the hydrocarbon. Several washes of the aqueous phase with hexane usually reduced the impurity to a level which gave an equivalent weight within 10% of the theoretical. For purposes of this study we arbitrarily established this as an acceptable level. We found that it was also possible to convert the amidine to the free base, in which form it preferred the pentane or hexane phase. Successive washes of this phase with ethanol-water also removed the undesirable impurity. The former procedure was preferable, since the crude product is then obtained in the hydrochloride form, in which form it is less susceptible to hydrolytic decomposition.

Table II

Properties of Amides

Compound	Notebook Reference	Yield		Elemental Analysis		
				C	H	N
N-(2-ethylhexyl)-2-ethylhexanamide	GW-48-68: 107+140	92-5%	Found	75.5	12.7	5.8
			Calc	75.2	13.0	5.5
2-ethylhexyl-p-t-butylbenzamide	GW-48-68:132	-	Found	78.5	10.6	4.5
			Calc.	78.9	10.8	4.8
n-octyl-n-octanamide	GW-48-68:133	72%	Found	75.9	12.5	5.4
			Calc.	75.2	13.0	5.5
N-(2-ethylhexyl)-n-octanamide	GW-48 68:145	-				
N(2-ethylhexyl)-neodecanamide	GW-1-70:53	95%				
N-Dodecylneodecanamide	GW-1-70:48	75%				
N-Octyl-2-ethylhexanamide	GW-19-70:68	89%				
N-Dodecyl-2-ethylhexanamide	GW-1-70:43	61%				

One amidine was prepared by a different route, involving the addition of a Grignard reagent to dicyclohexyl carbodiimide, as follows:



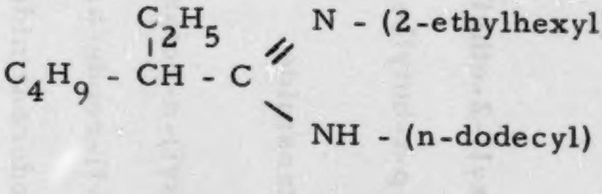
(13)

(14)

The carbodiimide happened to be a convenient material at the time it was done, but the carbodiimides are no longer commercially available. For all other syntheses we have therefore used the imidoyl chloride method.

The various amidine hydrochlorides prepared in this study are listed in Table III. Detailed synthesis procedures for each of the methods used are given in the Appendix.

Because of the awkwardness of using the full names of these compounds, we have resorted to a shorthand description of them, as follows. Aliphatic substituents are denoted by a two-letter abbreviation; e.g., octyl = Oc, dodecyl = Do. For amidines the two substituents on the nitrogen are given first, followed by the designation of the carboxylic acid chain, and the capital letter A to denote the amidine structure. For example, N-(2-ethylhexyl)-N'-(n-dodecyl)-2-ethylhexanamidine the structure of which is



is designated as DoEhEhA, where Eh denotes 2-ethylhexyl, and Do denotes n-dodecyl.

Table III

Properties of Amidines

Compound	Shorthand Designation	Notebook	Approx. Yield		Elemental Analysis				Equivalent Weight
					C	H	N	Cl	
N, N' Dicyclohexyl nonanamidine, hydrochloride	Cy_2NoA	GW 48-68:12	20%	Found	70.8	11.6	7.6	8.6	Found 412
				Calc	70.7	11.6	7.8	9.9	Calc 357
N, N' di(2-ethylhexyl)-2-ethylhexanamidine	Eh_2EhA	GW 48-68:125	22%	Found	79.4	13.4	7.5		Found 391
				Calc	78.7	13.7	7.6		Calc 367
		GW 1-70: 28	64%						Found 388
									Calc 367
N-(2-ethylhexyl)-N'-(n-octyl)-2-ethylhexanamidine, hydrochloride	EhOcEhA	GW 48-68:142	20%	Found	71.9	12.8	7.0	8.3	Found 427
				Calc	71.5	12.8	6.9	8.8	Calc 403
N, N'-di(2-ethylhexyl)n-octanamidine, hydrochloride	Eh_2OcA	GW 48-68:146	22%	Found	72.0	13.0	6.8	8.0	Found 442
				Calc	71.5	12.8	6.9	8.8	Calc 403
N-di(n-Butyl)-N'-(2-ethylhexyl)-2-2-ethylhexanamidine	(Bu_2)EhOcA	1-70:13	29%						Found 378
									Calc 367
N-Dodecyl-N'-(2-ethylhexyl)-2-ethylhexanamidine, hydrochloride	DoEhEhA	1-70:21	60%	Found	73.5	12.7	6.3	7.4	Found 480
				Calc	73.2	13.0	6.3	7.8	Calc 460
N-Dodecyl-N'-(2-ethylhexyl)-neodecanamidine	DoEhNdA	1-70:51	35%	Found	80.4	13.7	6.2		Found 483
				Calc	80.2	13.7	6.2		Calc 450

Guanidines will be denoted in the same way, except that, since all of the nitrogen atoms are equivalent, the order of stating the substituent groups is immaterial. The compound N, N'-dioctyl-N''-(2-ethylhexyl) guanidine is denoted Oc_2EhG.

While most yields shown in the table are relatively low, this is at least partly the result of losses during the partitioning and workup procedures. Actual yields of crude product would be significantly higher, but we did not attempt to determine them.

One cause of low yield was presumably side reactions, of which one is that shown in equations 10 and 11. We did not attempt to identify these impurities, although we were able to identify considerable amounts of the starting amide in some products. In later preparations, the reaction time in both stages was increased, with a corresponding increase in yield.

In addition to the elemental analysis and equivalent weight, the infrared scans of the products were obtained, and in a few cases, proton magnetic resonance scans were obtained, to confirm the structures.

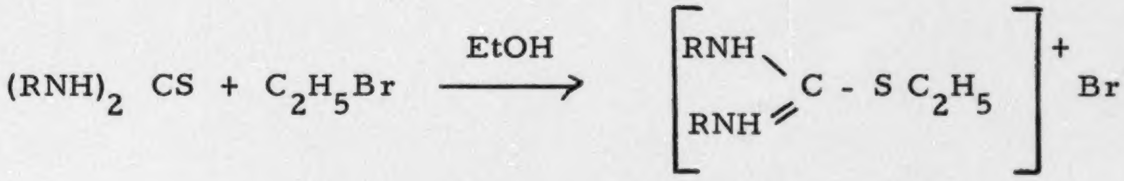
Both chloride and equivalent weight determinations were made titrimetrically in a water-acetone medium. Chloride was determined by titration with silver nitrate in the standard manner. Equivalent weights were determined by first converting a sample of the compound, dissolved in a diluent, to the free base by contact with dilute sodium hydroxide. Titration with standard acid gave not only the equivalent weight, but also an indication of the presence or absence of the excess free aliphatic amine used in the final reaction step. Because of its much weaker basicity presence of this material showed up as a shoulder on the titration curve of the amidine.

The amidines prepared here were all pale yellow or colorless liquids at ambient temperatures. The hydrochlorides, however, were extremely viscous liquids, also pale yellow or colorless, with the consistency of molasses. The one exception to this was the dicyclohexyl analog, which was obtained as the bromide salt, and was a white crystalline solid. During the course of this work, none of the liquid hydrochlorides showed any tendency to crystallize.

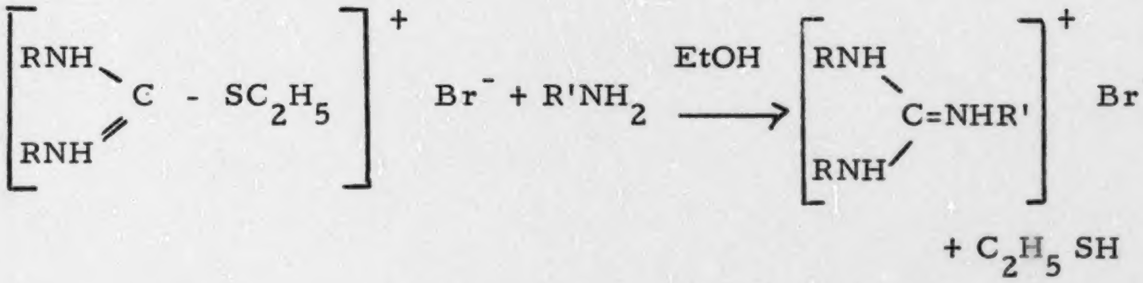
Guanidines

The most convenient and versatile laboratory synthesis of substituted guanidines involves conversion of a substituted thiourea to the S-alkyl thiuronium salt, and subsequent conversion of this intermediate to the guanidine (44, 45). If the desired thioureas are not available, they can be readily prepared from carbon disulfide and amines (46). The reactions are:

$$2\,RNH_2 + CS_2 + NaOH \xrightarrow[\Delta]{H_2O} (RNH)_2CS + NaHS + H_2O \qquad (15)$$



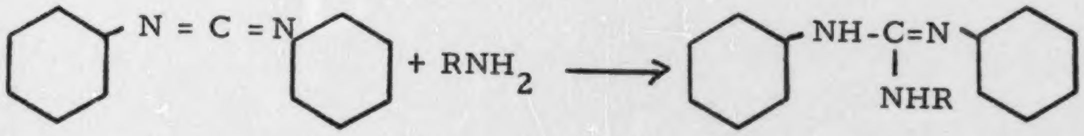
$$(RNH)_2\,CS + C_2H_5Br \xrightarrow{EtOH} \left[\begin{array}{l} RNH \diagdown \\ \qquad C - S\,C_2H_5 \\ RNH \nearrow\!\!\!\nearrow \end{array}\right]^+ Br^- \qquad (16)$$



$$\left[\begin{array}{l} RNH \diagdown \\ \qquad C - SC_2H_5 \\ RNH \nearrow\!\!\!\nearrow \end{array}\right]^+ Br^- + R'NH_2 \xrightarrow{EtOH} \left[\begin{array}{l} RNH \diagdown \\ \qquad C{=}NHR' \\ RNH \diagup \end{array}\right]^+ Br^- + C_2H_5SH \qquad (17)$$

Relatively good yields were obtained for all three steps. The final product was subjected to the partitioning procedure described in the amidine synthesis section, in order to improve the quality of the product.

One additional synthesis involved the use of N, N'-bis-(cyclohexyl) carbodiimide, which was available at that time. Formation of a guanidine occurs rather simply by reaction with an amine, as follows:



The guanidines prepared by these methods are listed in Table IV. Detailed synthesis procedures are given in Appendix I. These materials were usually obtained as the hydrobromides, but both bromides and chlorides were waxy solids or extremely viscous liquids. None were soluble in toluene to the extent of 0.1 molar. Since the amidines appeared to be suitable materials, the synthesis of additional guanidines was discontinued.

PHYSICAL CHEMISTRY OF THE AMIDINE EXTRACTION SYSTEMS

Prior to the start of this study we had planned to examine both amidines and guanidines as potential extractants. As events have developed, we have confined our work almost entirely to the amidines for two major reasons. First, initial experiments with the amidines indicated they fulfilled all of the requirements which we had set forth for such materials. Second, the few guanidines which we prepared turned out to be insoluble in toluene (in the hydrobromide form) at the level of 0.1 M, which we considered to be a rough lower limit for practical consideration. Solubility is observed at very high guanidine salt concentration (above about 60-70%), but the solutions are quite viscous, and of uncertain value in the systems of interest. We have since found that these materials are soluble in toluene containing various polar additives (e.g., alcohols). Conceivably, the nitrate/chloride selectivity could be greater than for amidines, but we have no data on this point.

Basis of the Experimental Methods

Apparent Basicity of the Amidines. One of the critical requirements for the extractant in the systems under study is that it should be a sufficiently strong base to exist as the salt form in contact with neutral aqueous solutions. We have used the apparent acid dissociation constant of the amine salt as a convenient measure of the relative acid strength of the protonated amidine. This quantity is defined by equation 6. The term "apparent" is applied here because the thermodynamic activities of the free base and the amidine salt in the organic phase are not known. We have, in fact, shown that in the analogous aliphatic amine systems, the amine salt is extensively aggregated (34), so that the simple buffer equation defining K_a is not obeyed; that is, K_a is not a constant. Nevertheless, the apparent acid constant is a useful parameter for expressing the relative behavior of the various compounds and their sensitivity to certain variables of interest. The physical significance of K_a is most easily appreciated by converting equation 6 to the logarithmic form

$$pK_a = pH + \log \frac{\overline{(BHCl)}}{\overline{(B)}} + \log (Cl^-) \qquad (15)$$

From this equation it can be seen that the pK_a is the pH of the aqueous phase when the organic phase contains equal concentrations of the salt and free base form, and when the aqueous phase is 1 molar

Table IV

Properties of Guanidines

Compound	Notebook Reference	Approx. Yield		C	H	N	Halide, X	Equivalent Weight
N-(Primene 81R)-N', N'' di(o-tolyl) guanidine, hydrochloride	GW-48-68:41	25%	Found	74.9	9.1	8.1	6.7	Found 526
			Calc	73.4	9.7	9.2	7.7	Calc 458
N, N' dioctyl-N'' butylguanidine, hydrobromide	GW-48-68:90	-	-	-	-	-	-	-
N, N', N'' Trioctyl guanidine, hydrobromide	GW-48-68:93	-	Found	63.7	11.8	8.8	16.1	Found 497
			Calc	63.0	11.2	8.9	16.9	Calc 476
N-(2-ethylhexyl) -N, N''-dioctyl guanidine, hydrobromide	GW-48-68:94	-	Found	63.9	11.5	8.8	16.3	Found 490
			Calc	63.0	11.2	8.9	16.9	Calc 476
N, N', N''-tris(2-ethylhexyl) guanidine, hydrobromide	GW-48-68:105	75%	Found	63.3	11.3	9.0	16.1	Found 496
			Calc	63.0	11.2	8.9	16.9	Calc 476
N(Phenethyl)-N', N''-di(2-ethylhexyl)guanidine, hydrobromide	GW-1-70:59	75%	-	-	-	-	-	Found 498
								Calc 468

(more accurately, unit activity) in the counter anion. Because our interest lay in the potential application of these systems to waste waters, we chose to make measurements in a standard system containing 0.010 M sodium chloride. This concentration, which is equivalent to 585 ppm of sodium chloride, is more typical of the dissolved solids concentration in municipal sewage. By making the appropriate substitutions in equation 16 we can still determine the pK_a for the amidine system under study.

Ion Selectivity. Removal of nitrate from waste waters by the proposed process is based on exchange of nitrate in the water for some other ion in the organic phase. Since several other ionic species will be present in most waste water systems, and since nitrate will be one of the minor species, it is important, obviously, that the extractant system have a relatively high affinity for nitrate ion as compared with other ionic species. Based on experience with analogous aliphatic amine extraction systems (32, 33) we expected the major interference to come from chloride ion, and our screening experiments were based on determining the selectivity for nitrate over chloride ion. The selectivity constant was defined in equation 3, and was the parameter determined in screening for this property.

Other major ionic constituents of waste water include both bicarbonate and sulfate ions, and selectivites involving these species were determined in one case.

Soluble Loss of Extractant to Aqueous Phase. A major concern in extraction systems is the loss of the extractant to the aqueous phase. In the type of exchange systems of interest here we expect the soluble loss to consist mainly of the salt form of the extractant, due to its greater polarity. The distribution of extractant between organic and aqueous phase will presumably be governed by the equilibrium

$$BH^+ + Cl^- \rightleftharpoons \overline{BHCl} \; ; \qquad K_s = \frac{\overline{(BHCl)}}{(BH^+)(Cl^-)} \qquad (16)$$

In other words, the loss of the amidinium ion should be dependent upon the concentrations of anions in the aqueous phase, higher concentrations tending to drive the organic cation back into the organic phase. Data were obtained with the idea of determining the equilibrium constant for equation 16 as a means of comparing different compounds and of predicting losses under various conditions.

Experimental Methods

In addition to the compounds synthesized in this project, two commercial aliphatic amines were included in the physical chemistry study. Primene JM-T is a highly branched primary amine, in which the amino group is attached to a tertiary carbon atom. Its equivalent weight indicates it to contain about 21 carbon atoms. Amberlite LA-2 is a secondary amine obtained by attaching a dodecyl group to the nitrogen atom of a lower molecular weight analog of JM-T. Its equivalent weight indicates a total of about 26 carbon atoms.

Three hydrocarbon diluents were used in the studies. The toluene was a standard material. Chevron 3 is a high boiling aromatic hydrocarbon diluent obtained from the Standard Oil Company. The boiling range midpoint is about 188°C and is stated to contain 100% aromatic compounds. Cyclosol 73 is a product of Shell Oil Company with a boiling range midpoint of 218°C, and is stated to contain 74% aromatics, 10% naphthenes, and 16% aliphatics.

All experiments were carried out at ambient (about 22 ± 2 °C) temperature. Aside from certain special procedures, described below, analytical techniques involved mainly conventional procedures. Water was determined by the Karl Fischer titration. Chloride was determined by titration with silver nitrate for higher levels, and by coulometric titration for lower ones. Titrations of organic phases for either chloride or for equivalent weight were done potentiometrically in an acetone/water medium.

Apparent pK_a of Extractants. A 0.5 M solution of the amidine was first titrated in acetone-water solution to determine its exact concentration. Dilutions were made to four additional concentrations. These solutions were shaken 30 minutes with twice their volumes of 0.010 M aqueous NaCl solutions, each of which contained a known amount of hydrochloric acid. In most experiments this was equal to half of the total amidine, thus producing a system containing equal concentrations of free base and salt form of the amidine. In some experiments variable quantities of acid were added to achieve other free base/salt ratios. After equilibration of the phases, pH was read directly in the aqueous system, and the phases were centrifuged, if necessary, and separated. Total aqueous chloride was determined by coulometric titration, and the other quantities were calculated by difference from initial values.

Soluble Loss of Extractants. A 0.1 M solution of the amidine hydrochloride was shaken 30 minutes with 0.010 M NaCl solution. The aqueous phase was analyzed for amidine, using the picrate method. This method is based on the extraction of the picrate salt of an alkylammonium cation into chloroform, followed by determining the absorbance of the yellow picrate ion in the chloroform. The aqueous phase is buffered at about pH 3 in order to ensure the existence of the amine component in its cationic form. The procedure is described in detail in Appendix II.

At least two successive contacts of the organic phase with 0.010 M sodium chloride were made to ensure that successive losses were equal. This procedure is often necessary when dealing with impure materials, since an impurity which is more soluble in water than the principal compound would appear in initial contacts, and give a false result. Successive contacts, however, can be used to wash such impurities out. When successive contacts give the same or nearly the same results, it can be assumed that the impurity has been eliminated, and the observed values of loss can be identified with the principal compound. Following this procedure, portions of the 0.1 M amidine salt solution were shaken with 0.03, 0.1, and 0.3 M sodium chloride, and the soluble losses were determined.

Loss of the hydrocarbon diluent was determined by shaking the straight diluent with several successive portions of 0.010 M sodium chloride, separating and either filtering or centrifuging the aqueous phase. The soluble diluent was determined in one method by extracting the aqueous phase with 1/25 of its volume of carbon disulfide and determining the diluent content by gas-liquid chromatography. A second method involved back extraction with cyclohexane instead of carbon disulfide, followed by determination of the ultraviolet absorbance of the cyclohexane solution.

Ion Selectivity of Amidines. A 0.25 M solution of the free amidine base was titrated to determine the exact concentration. Portions of the solution were converted separately to the chloride and nitrate or other salt by shaking with the corresponding aqueous acid. These salt solutions were mixed in varying proportions and shaken 30 minutes with an equal volume of 0.010 M sodium chloride. After separation, the organic phases were stripped with 1 M sodium hydroxide for analysis. Both the equilibrium aqueous phase and the strip solution were analyzed for nitrate by two methods. Chloride was determined only in the strip solution, by titration with silver nitrate.

Nitrate was determined by the Hach method and the modified brucine method (47). The Hach method involved the use of a Hach nitrate water testing kit, based on reduction of nitrate to nitrite, diazotization and dye formation. Instead of the color comparator, we determined absorbance with a standard spectrophotometer. Some difficulty was occasionally encountered with the formation of cloudiness, which of course tended to give slightly high results, and in some cases, prevented use of this method.

The modified brucine method was also used, in order to have an independent check on the nitrate values. We have in the past had difficulty with this and similar methods using strong acid media, which we attributed to reaction of traces of organic materials with the nitrate in the strong acid medium. This phenomenon produces low results. While the Hach and brucine methods generally agreed fairly well, deviations were generally in the directions expected.

Determination of nitrate/bicarbonate selectivity required somewhat more care. It was necessary to carry out the experiment at a pH of 8 to 8.5, the approximate pH of a bicarbonate solution, in order to ensure the absence of free carbon dioxide, which would interfere. This pH restruction necessitated using an amidine solution which was only partly in the salt form. Bicarbonate was determined in the equilibrium aqueous phase simply by titration with acid. Determination of bicarbonate in the organic phase involved stripping with sodium hydroxide, and titration with acid in the usual manner.

Results and Discussion

pH Dependence of the Extractant. Values of the pK_a of the amidines are shown in Figure 1 as a function of the concentration of the amidine salt in the organic phase. The value of pK_a varies considerably over the range studied, and equation 6, in which K_a is assumed to be constant, is clearly not obeyed in this region. Tabular data from which this curve and other pK_a curves were obtained is given in Appendix III.

We have shown in earlier studies that in aliphatic amine systems the same phenomenon is observed, and is due to aggregation of the salt form of the extractant (34). It is possible, however, by plotting the apparent pK_a against the concentration of the salt form, to obtain information about the aggregation process. If one assumes the existence of only one aggregated species, in addition to the monomeric form of the salt, the following equation can be derived (34):

$$pK_a = \text{constant} + \frac{n-1}{n} \log \overline{(BHCl)}_{\text{Total}} \qquad (17)$$

where n refers to the number of monomeric units in the aggregate, and $(BHCl)_{Total}$ denotes the total concentration of all forms of the hydrochloride; i.e., the analytical concentration of the salt. Thus, a plot of $\overline{(BHCl)}_{Total}$ against pK_a gives a line of slope $\frac{n-1}{n}$. Besides the assumption of a single aggregated species, the equation also assumes no interaction between salt and free base, and also assumes that activity coefficients in the organic phase are constant throughout the range of data.

The curves in Figure 1 all exhibit a rather pronounced positive slope, indicative of considerable aggregation. Some exhibit a definite curvature, with the slope at the upper end being decidedly greater than 1. A slope of 1, it should be noted, indicates an infinite aggregate. We believe that this is probably due to the fact that concentrations are so high in this region that the various assumptions enumerated in the preceding paragraph are simply not obeyed. Considering the limited range of data, we believe that aggregation is clearly occurring, but that quantitative conclusions about the aggregation process are unwarranted.

Another indication of the lack of strict adherence to the assumptions of equation 6 is given by the data of Figure 2. We have shown here pK_a data for two systems, Eh_2EhA and DoEhEhA, each taken in two different ways. One curve of each pair was obtained from systems where the base/salt ratio in the organic phase was kept at 1.0; the second of each pair was taken from systems where the total amidine concentration was constant, the ratio of base/salt being varied. Although there is general agreement between the two curves of each pair, there is significant divergence at the lower ends of the curves, indicating that the variable free base concentration exerts some effect on the equilibrium.

In spite of the difficulties in explaining precisely the origin and magnitude of the deviations from equation 6 we believe the important point is that the pK_a of a particular compound is a function of the concentration of the salt form of the extractant, and that this concentration must be considered in working with the physical chemistry of these systems. A corollary is that the ability to vary the concentration of the extractant in a system provides an additional degree of freedom in achieving the desired basicity in an extractant system.

Of considerably greater interest, however, is the effect of molecular structure on the apparent basicity of the compounds. The earlier work with aliphatic amines led to the observation that increasing the steric hindrance around the nitrogen atom decreased the apparent base strength of the amine. An increase in the steric hindrance

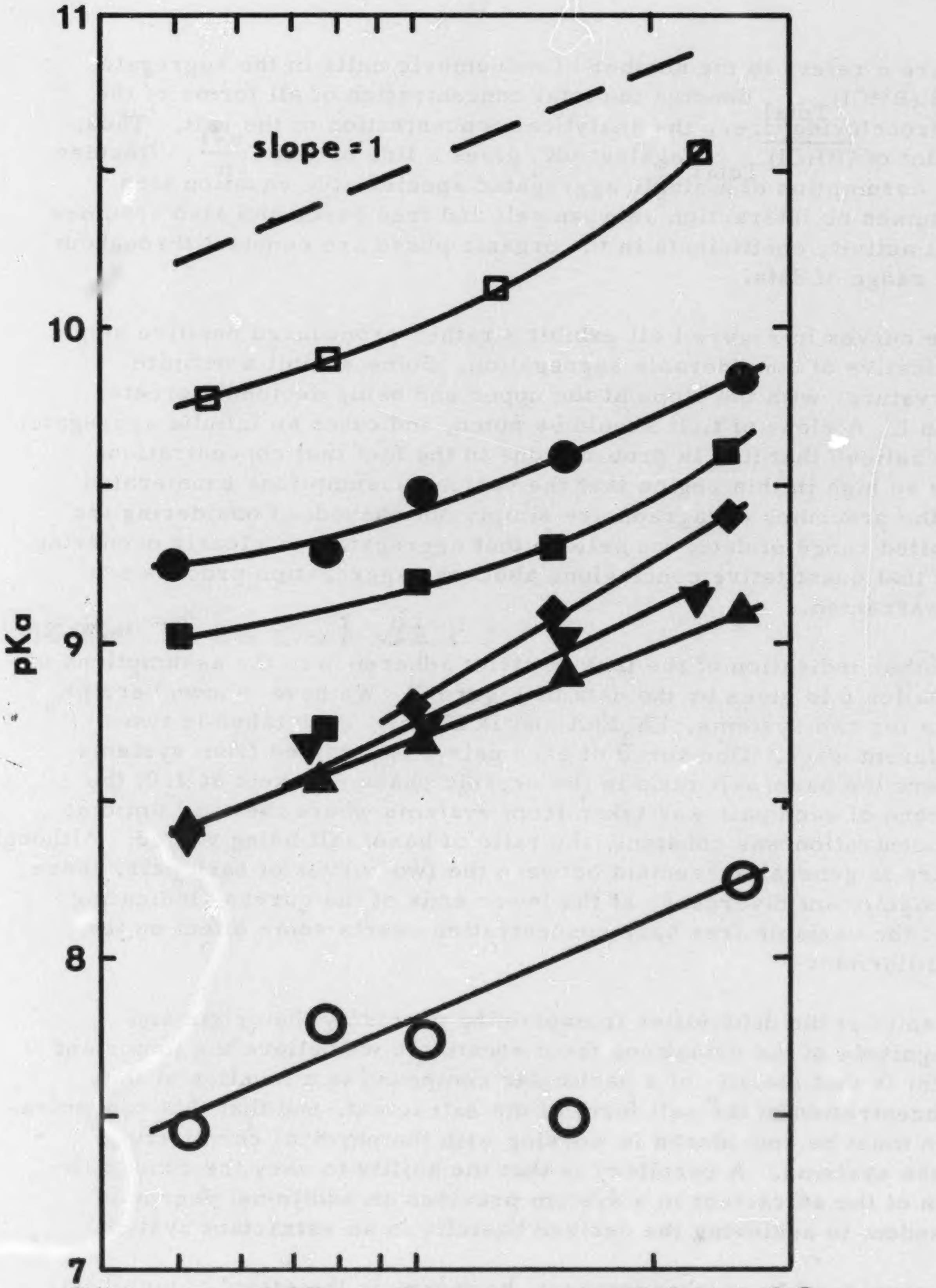


Figure 1. Apparent pK_a of Amidines

Ratio $\overline{(B)}/\overline{(BHCl)} = 1.0$;
Aqueous phase, 0.010 M $NaNO_3$.
Slope of dotted line = 1.0.

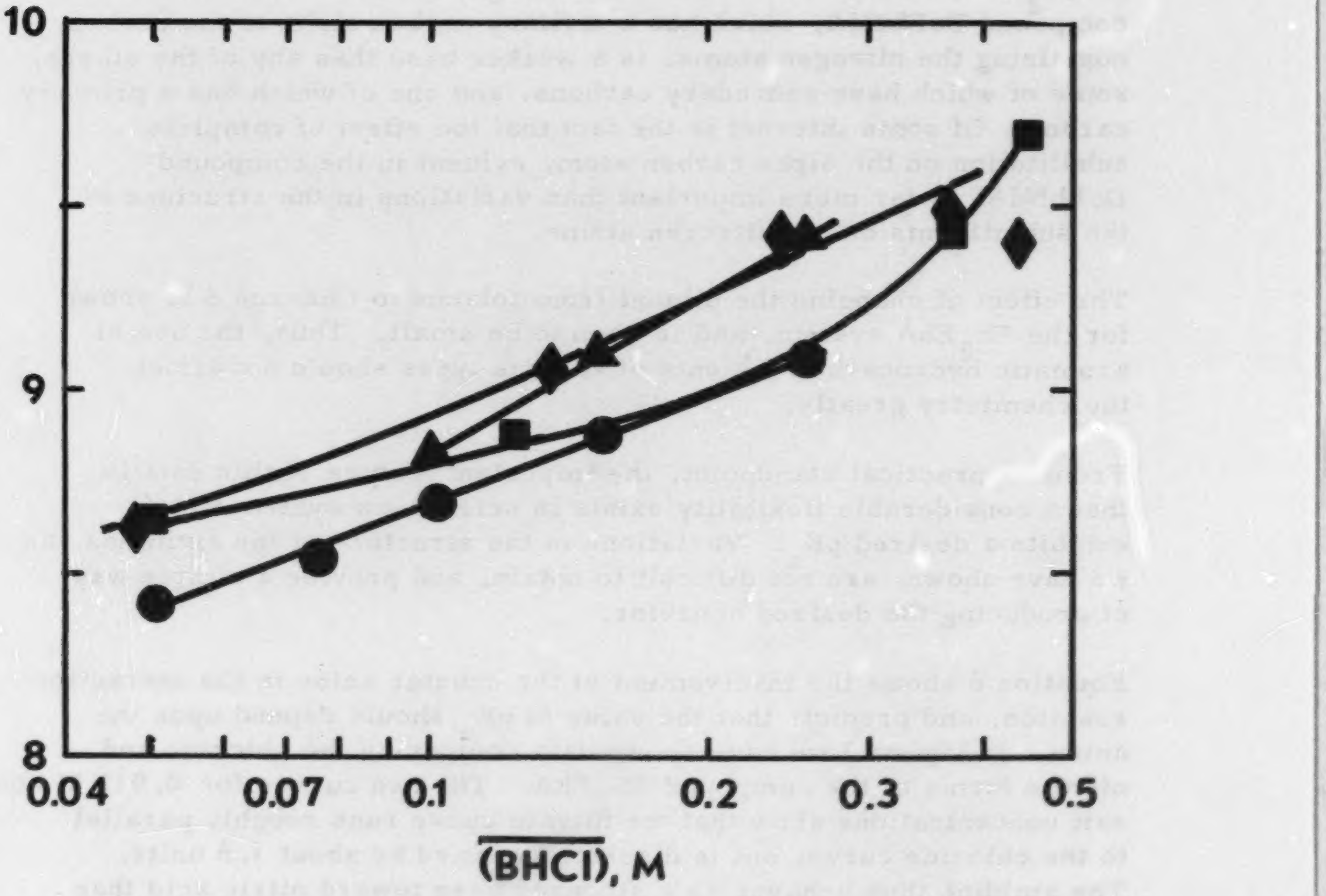


Figure 2. Apparent pK_a values of Amidines

Aqueous phase, 0.010 M NaCl; diluent, Chevron 3.

■ Eh_2EhA, $\overline{(B)} + \overline{(BHCl)} = 0.5$ M
● Eh_2EhA, $\overline{(B)}/\overline{(BHCl)} = 1.0$
◆ DoEhEhA, $\overline{(B)} + \overline{(BHCl)} = 0.48$ M
▲ DoEhEhA, $\overline{(B)}/\overline{(BHCl)} = 1.0$

increases the difficulty of forming a stable aggregate involving the highly polar parts of the molecule, with the result that the salt form is destabilized. This is equivalent to saying that the compound behaves as a weaker base.

The same phenomenon appears to exist in the amidine series. For example, the compound Eh$_2$EhA, in which all chains are branched, is a weaker base (stronger acid, or lower pK$_a$) than either EhOcEhA or Eh$_2$OcA, both of which have one straight chain the molecule. The compound DoEhNdA, which has a tertiary carbon alpha to the carbon containing the nitrogen atoms, is a weaker base than any of the others, some of which have secondary carbons, and one of which has a primary carbon. Of some interest is the fact that the effect of complete substitution on the alpha carbon atom, evident in the compound DoEhNdA, is far more important than variations in the structure of the substituents on the nitrogen atoms.

The effect of changing the diluent from toluene to Chevron 3 is shown for the Eh$_2$EhA system, and is seen to be small. Thus, the use of aromatic hydrocarbon diluents of various types should not affect the chemistry greatly.

From a practical standpoint, the important feature of this data is that a considerable flexibility exists in selecting a system which exhibits a desired pK$_a$. Variations in the structure of the amidines, as we have shown, are not difficult to obtain, and provide a simple way of producing the desired behavior.

Equation 6 shows the involvement of the counter anion in the extraction reaction, and predicts that the value of pK$_a$ should depend upon the anion. In Figure 3 we have shown data comparing the chloride and nitrate forms of the compound Eh$_2$EhA. The two curves for 0.919 M aqueous salt concentrations show that the nitrate curve runs roughly parallel to the chloride curve, but is displaced upward by about 1.6 units. The amidine thus behaves as a stronger base toward nitric acid than toward hydrochloric acid, or, to put it another way, the amidinium ion in the organic phase has a greater affinity for the nitrate ion than the chloride ion. The ion selectivity, S, can be derived from this data by writing equation (6) in both the nitrate and chloride forms, and then dividing one by the other. We get

$$S = \frac{\overline{(NO_3^-)}\,(Cl^-)}{(NO_3^-)\,\overline{(Cl^-)}} = \frac{K_a^{NO_3}}{K_a^{Cl}} \qquad (18)$$

which is simply equation 3 by which we defined the selectivity. From this we can get

$$\log S = pK_a^{NO_3} - pK_a^{Cl} = 1.6 \qquad (19)$$

from which S is found to be about 40. Again, this equation makes certain assumptions, mainly that there is no interaction between the organic nitrate and chloride salts. Experimental determination of the selectivity by direct exchange experiments gives somewhat lower values, as we shall see.

The second pair of curves in Figure 3 was obtained with an aqueous phase composed of ammonia and ammonium nitrate to simulate the type of solution in a stripping system. The raw data are shown, but because activity coefficients at 1.0 M aqueous salt solutions are significant, the data were also corrected by applying the activity coefficients for ammonium nitrate to nitric acid in equation 6. This is not a strictly proper use of activity coefficients, since the activity coefficient of nitric acid in ammonium nitrate will be somewhat different from the coefficient for ammonium nitrate itself. The mixed activity coefficients were not available, and the resulting agreement of the two nitrate system curves is to some extent coincidental.

The suitability of these systems to waste water processing can be examined by first remembering that most natural waters, as well as municipal sewage, will exhibit a pH in the range of 7 to 8, which is maintained by the action of the carbon dioxide-bicarbonate buffer system. The pH of such systems can be raised somewhat by aeration to remove carbon dioxide, which will result in a pH approaching that of a bicarbonate solution, about 8.0 to 8.5. Similarly, the pH can be readily lowered by carbonation. The behavior of two of the extractant systems shown in the previous figures are replotted in Figure 4 in the form of titration curves; i.e., pH is plotted as a function of the ratio of salt and base forms of the extractant. We have also shown similar curves obtained with Primene JM-T, a primary amine, and Amberlite LA-2, a secondary amine. As we indicated earlier, these aliphatic amines behave as relatively weak bases in liquid-liquid systems, and under the conditions shown are almost entirely in the free base form at pH 7. In contrast, the two amidines,

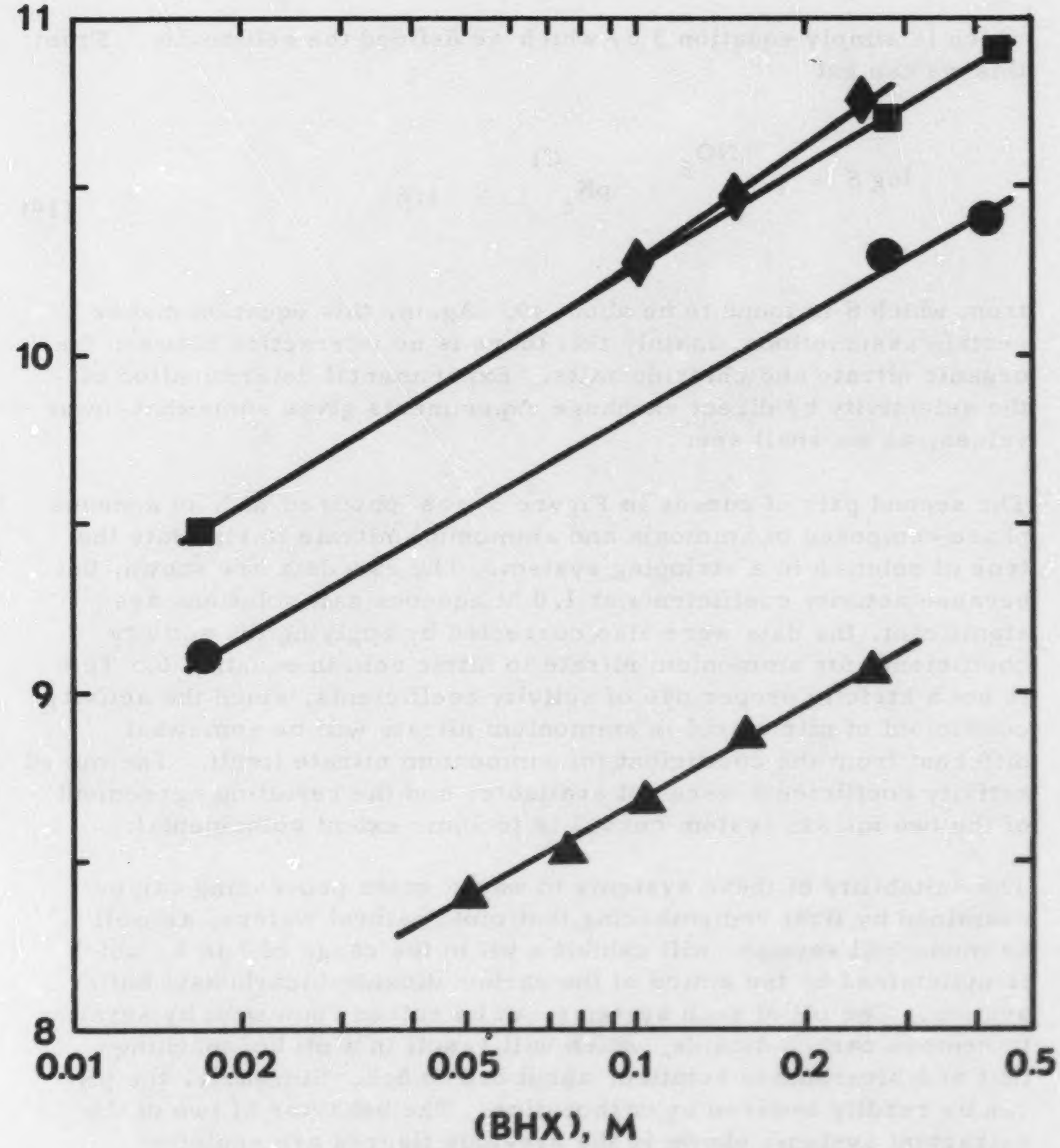


Figure 3. pK_a for Eh_2EhA in Chevron 3.

▲ aqueous phase, 0.010 M NaCl; $\overline{(B)}/\overline{(BHCl)} = 1.0$

◆ aqueous phase, 0.010 M $NaNO_3$; $\overline{(B)}/\overline{(BHCl)} = 1.0$

● aqueous phase, 1.0 M ammonium (hydroxide + nitrate); organic phase, 0.5 M Eh_2EhA in Chevron 3.

■ same, but data corrected for aqueous activity effects.

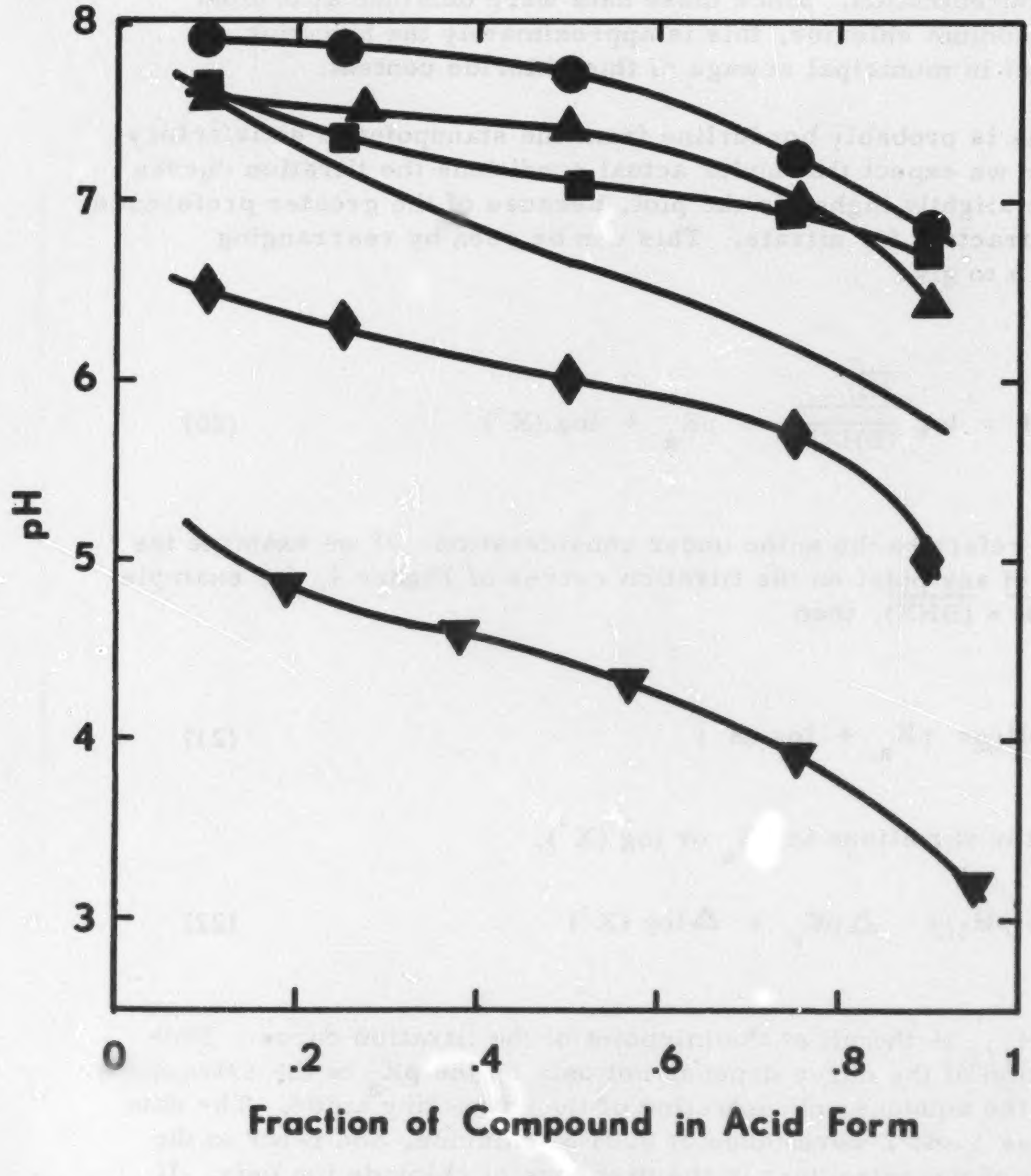


Figure 4. Effect of pH on Extractant Form.

Aqueous phase, 0.01 M NaCl; diluent, Chevron 3.

● 0.86 M DoEhEhA
▲ 0.49 M DoEhEhA
■ 0.50 M Eh_2EhA
▼ 1.12 M Amberlite LA-2
◆ 1.19 M Primene JM-T
Curved line, calculated for 0.005 M $NaHCO_3$

Eh_2EhA and DoEhEhA, are mainly in the hydrochloride form at pH 7, with the latter compound being about 85% in this form at its higher concentration. Since these data were obtained at 0.010M aqueous sodium chloride, this is approximately the behavior we can expect in municipal sewage of this chloride content.

While this is probably borderline from the standpoint of satisfactory operation we expect that under actual conditions the titration curves would lie slightly higher in the plot, because of the greater preference of the extractant for nitrate. This can be seen by rearranging equation 6 to give

$$pH = \log \frac{\overline{(B)}}{\overline{(BHX)}} + pK_a + \log (X^-) \qquad (20)$$

where X refers to the anion under consideration. If we examine the position of any point on the titration curves of Figure 4, for example where $\overline{(B)} = \overline{(BHX)}$, then

$$pH_{1/2} = pK_a + \log (X^-) \qquad (21)$$

and for any variations in pK_a or $\log (X^-)$,

$$\Delta pH_{1/2} = \Delta pK_a + \Delta \log (X^-) \qquad (22)$$

where $pH_{1/2}$ is the pH at the midpoint of the titration curve. Thus the location of the curve depends not only on the pK_a of the extractant, but also the aqueous concentration of the extracting anion. The data of Figures 1 and 2 were taken at 0.01 M chloride, and refer to the condition of the extractant in the presence of chloride ion only. If we consider a waste water with 0.001 M nitrate ion (about 62 mg nitrate/l.), and note that Figure 3 indicates a higher pK_a for nitrate by about 1.6 log units, we have

$$\Delta pH_{1/2} = 1.6 + \log \frac{(0.001)}{(0.01)} = 0.6 \qquad (23)$$

Thus, we expect the nitrate titration curve to lie about 0.6 pH unit higher than the chloride curve. The value of 1.6 for Δ pK$_a$ implies, as we discussed earlier, a selectivity for nitrate over chloride of about 40. In actual exchange experiments values closer to 20 have been observed, so that the Δ pH' expected in an operating system may be less than 0.6, perhaps only half of this figure.

Furthermore, the variation available in the apparent pK$_a$ of these materials, illustrated by the data in *Figure 1*, makes it clear that a compound with a higher pK$_a$ could be easily prepared. We chose to concentrate our studies on the two compounds Eh$_2$EhA and DeEhEhA because a compromise may be necessary to allow stripping of the system with ammonia, and because carbonation or a relatively small amount of mineral acid could be used to reduce the pH to the necessary point for extraction.

In the stripping step, we must determine the pH required to convert the amidine into the free base form, in the presence of high nitrate concentrations. The pK$_a$ for nitrate systems is greater than for chloride, and the titration curve for a nitrate system will lie higher in the field than the chloride curves shown in *Figure 4*. In addition, we wish to obtain a relatively high concentration of nitrate, and the dependency dictated by equation 21 shifts the titration curve even further upward. A single set of experiments was done with Eh$_2$EhA and an aqueous phase of 1.0 M ammonium hydroxide, and the data are shown in *Figure 5*. Under these conditions, the titration curve for the Eh$_2$EhA lies at about the same point as the curve for the ammonium hydroxide/ammonium ion system. In other words, the strip equilibrium

$$\overline{BHNO_3} + NH_4OH \rightleftharpoons NH_4^+ + NO_3^- + \overline{B} + H_2O \qquad (24)$$

is a measurable one. This is also shown by examination of the equilibrium constant,

$$\frac{\overline{(B)}\ (NO_3^-)\ (NH_4^+)}{\overline{(BHNO_3)}\ (NH_4OH)} = K_s = \frac{K_1\ K_a}{K_w} = 1.8 \times 10^9\ K_a \qquad (25)$$

where K$_1$ is the ionization constant of ammonium hydroxide, 1.8×10^{-5}, and K$_w$ is the ion product of water, 1.0×10^{-14}. From Figure 3

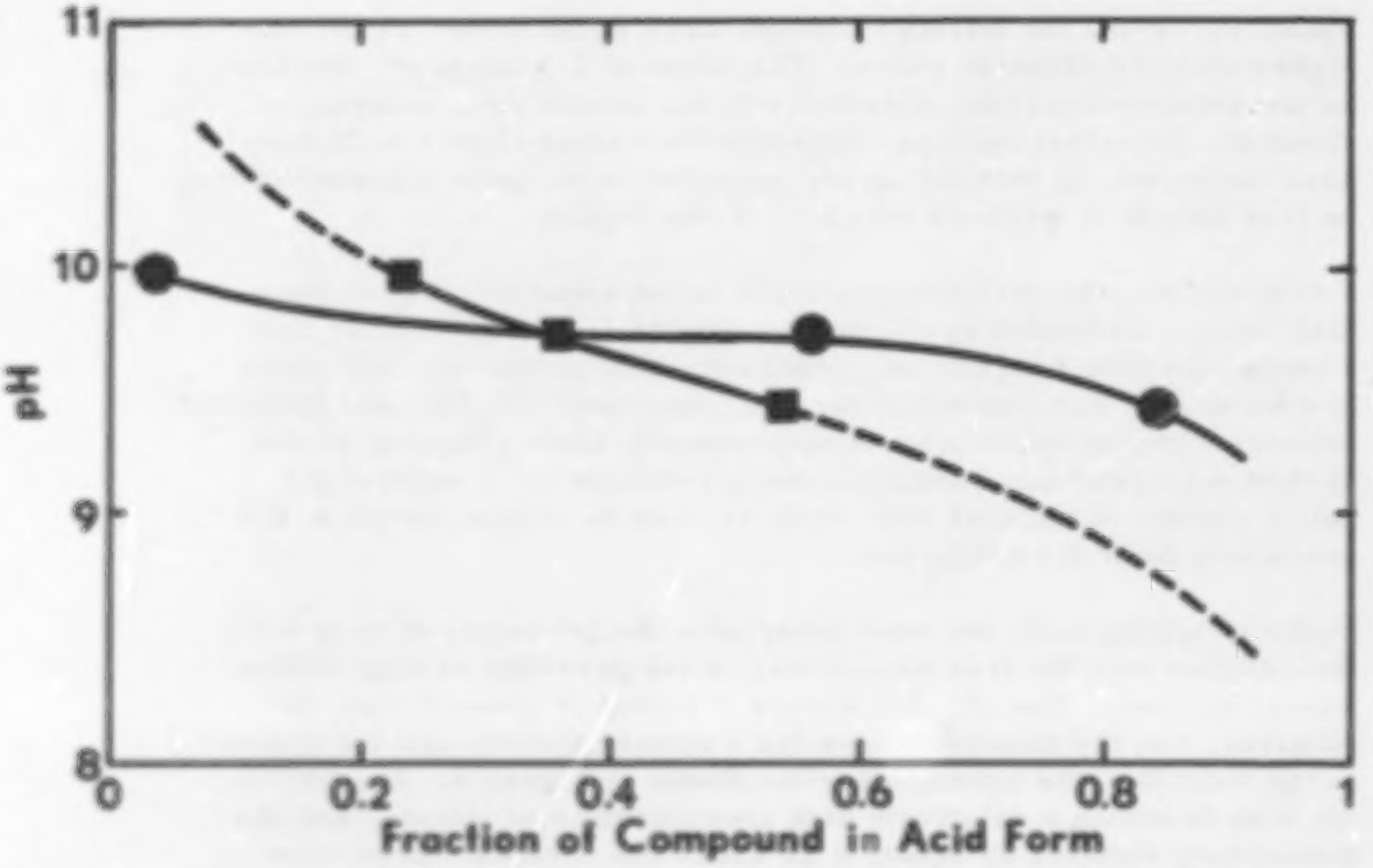


Figure 5. Effect of pH on Extractant Form.

Aqueous phase, 1.0 M ammonium (hydroxide + nitrate); Organic phase, 0.5 M Eh_2EhA in Chevron 3.

■ ammonium hydroxide/ammonium nitrate buffer system.

● Eh_2EhA system

we saw that pK_a for Eh_2EhA in the nitrate system varied from about 9 to 10.5 in the region studied. K_e thus varies from about 1.8 to 0.05, depending upon the ratio of free base/salt in the organic phase. From this equation, we can also readily predict that for stronger ammonia solutions (which would produce stronger nitrate solutions at equilibrium) the Eh_2EhA curve would lie still higher.

Thus, in the presence of nitrate ion at concentrations of 1.0 M or so, it is not possible to completely strip the nitrate from the extractant in a single contact. It is, of course, possible to do so by operating the strip countercurrently, wherein the entering ammonium hydroxide solution, containing no nitrate ion, contacts the nearly completely stripped extractant. In this way, a reaction with an equilibrium constant of unity can readily by pushed to completion.

We have not made a more detailed analysis of the ammonia strip because of the relatively small amount of data for this system. Ammonia was used in one of the column runs, however, and was found to be effective; the complete elution of the nitrate required considerable ammonia solution. It can be predicted that the use of a stronger alkali, such as sodium hydroxide or calcium hydroxide, should allow complete stripping to be accomplished in the presence of much higher nitrate concentrations. Time did not permit investigation of these systems, although these may be preferable to the use of ammonia.

Ionic Selectivity of Extractants. The data for nitrate/chloride selectivity are given in Table V for several of the amidines. Because of the disagreement between the two nitrate analytical methods, the precise values are subject to some uncertainty. The values generally fall in the range of 20-30, with no clear dependence upon either the ion composition of the organic phase, the diluent, or the particular extractant under study. The selectivity constant was determined for DoEhEhA at two extractant concentrations, 0.25 M and 0.89 M. Due to the variation between the two methods there appears to be no significant effect of the extractant concentration.

Selectivities for nitrate over sulfate, and for nitrate over bicarbonate, were determined only for the compound Eh_2EhA. The data are given in Tables VI and VII. The value of about 390 for nitrate/bicarbonate clearly indicates a high preference of the extractant cation for the nitrate. The value for sulfate of about 10^6, of course, is also quite high, but is not directly comparable, due to the more complex divalent/monovalent exchange reaction.

In order to study carbon dioxide, a contact was made between 0.25 M Eh_2EhA (nitrate salt form) in Chevron 3 and an aqueous phase containing 0.043 M $NaHCO_3$, 0.051 M $NaNO_3$, and 0.051 M CO_2.

Table V

Nitrate/Chloride Selectivity of Amidines

organic phase: 0.25 amidine in Chevron 3, except as noted
aqueous phase: 0.01 M mixed sodium salts

	Concentrations, M					
Compound	$\overline{(BHNO_3)}$	$\overline{(BHCl)}$	(NO_3^-)	(Cl^-)	$S_{Cl}^{NO_3}$	Analytical Method*
Eh_2EhA						
	0.224	0.053	0.00165	0.0083	21.3	(B)
	0.138	0.130	0.00047	0.0089	22.2	(B)
	0.058	0.206	0.00013	0.0095	21.5	(B)
DoEhEhA						
	0.198	0.047	0.0025	0.0127	21.4	(H)
			0.0023		23.3	(B)
	0.124	0.121	0.00072	0.0137	19.5	(H)
			0.00058		24.2	(B)
	0.050	0.196	0.00023	0.0136	15.6	(H)
			0.00011		31.5	(B)
DoEhEhA; $\overline{\text{(amidine)}}$ = 0.89 M						
	0.713	0.175	0.0023	0.0116	20.5	(H)
	0.664		0.0021		21.0	(B)
	0.448	0.433	0.00086	0.0146	17.6	(H)
	0.418		0.00073		19.3	(B)
	0.179	0.694	0.[illegible]27	0.0153	14.6	(H)
	0.169		0.00020		18.6	(B)
DoEhEhA; (Cyclosol 73)						
	0.197	0.045	0.0036	0.0151	18.4	(H)
			0.0031		21.1	(B)
	0.124	0.118	0.00099	0.0170	18.0	(H)
			0.00078		22.9	(B)
Eh_2OcA						
	0.190	0.048	0.0017	0.0090	20.9	(H)
			0.00175		20.3	(B)
	0.119	0.117	0.00049	0.0104	21.6	(H)
			0.00046		23.0	(B)
	0.048	0.185	0.00014	0.0117	21.7	(H)
					27.6	(B)
EhOcEhA						
	0.198	0.049	0.0019	0.0108	22.9	(H)
			0.00212		20.5	(B)
	0.124	0.120	0.00062	0.0134	22.4	(H)
			0.00064		21.5	(B)
	0.050	0.193	0.00018	0.0136	19.6	(H)
			0.000087		40.5	(B)

---

*H = Hach method; B = Brucine method

Table VI

Nitrate/Sulfate Selectivity of Amidines

Organic Phase: 0.25 M Eh_2EhA in Chevron 3;
Aqueous Phase: 0.020 N Mixed Sodium Salts

Concentrations, Normal				
$\overline{(BHNO_3)}$	$\overline{(B_2H_2SO_4)}$	(NO_3^-)	$(SO_4^=)$	$\log S^{NO_3}_{SO_4}$
0.256	0.00048	0.00092	0.020	6.51
0.255	0.0016	0.0019	0.058	5.81
0.256	0.0008	0.0012	0.099	6.74

Table VII

Nitrate/Bicarbonate Selectivity of Amidines

Initial Organic Phase: 0.12 M $Eh_2EhA \cdot HNO_3$, 0.24 M Eh_2EhA in Chevron 3. Initial Aqueous Phase, 0.10 M $NaHCO_3$

Equilibrium Concentrations, M

$\overline{(BHNO_3)}$	$\overline{(BH_2CO_3)}$	(NO_3^-)	(HCO_3^-)	$S^{NO_3}_{HCO_3}$
0.12	0.0033	0.0086	0.093	393

Phases were analyzed as before, and slightly more total carbon ($CO_2 + HCO_3^-$) was found in the organic phase than the aqueous. Since bicarbonate extraction should be quite small, the amount can be considered essentially all free carbon dioxide, and the distribution coefficient of this species is then 1.6. It is more realistic, we believe, to express this as a simple distribution coefficient instead of an exchange constant, since no ionic reaction is involved. The value of 1.6 is probably reasonable, since carbon dioxide is somewhat more soluble in most organic solvents than in water.

We can use the data reported above to predict the behavior of amidine systems in the treatment of a waste water. A typical composition was discussed in the proposal for this study, and is reproduced in Table VIII. From the mole ratios of ions in the water, and the selectivity constants determined above, we have calculated the expected composition of the organic phase after equilibration with the water. These values are also given in the table. It should be noted that the calculation for sulfate involves the organic nitrate concentration, because of the character of the divalent/monovalent exchange equilibrium. A value of 0.5 M nitrate ion was assumed in the organic phase.

The results clearly bear our the existence of chloride as the only significant interference. For this waste water, we expect the organic phase, and ultimately the nitrate waste, to consist of 88% nitrate ion and 12% chloride. For waters of higher total dissolved solids, of course, the chloride can also be expected to be higher, with a resulting higher chloride content of the nitrate containing waste.

Other ions which may be present in waste water include nitrite, phosphates, silicate, and to a minor extent, borate. The ionization constant of boric acid, 6.4×10^{-10}, and that of silicic acid, about 2×10^{-10}, suggest that little extraction of either element will occur, since both species will be present in most waste water as the undissociated acid. The possibility exists that both phosphate and nitrite would be picked up to some extent by the extractant, but this was not investigated.

One possible coextractant with nitrate ion is carbon dioxide. While it is not an ionic salt, it is soluble in most organic solvents, and the distribution coefficient of 1.6 which we reported above for a typical extractant system suggests that coextraction would certainly occur. On the other hand, the amount would probably be small. The titration curve for bicarbonate, shown in Figure 4, indicates that most dissolved carbon would probably be in the form of bicarbonate, varying from

Table VIII

Expected Extractant Composition from Treatment of Typical Waste Water[a]

Species	Typical Waste Water		Extractant Composition, for 0.5 M Eh_2EhA	
	mg/l	mole ratio X^-/NO_3^-	mole ratio X^-/NO_3^-	fraction of total ions
Chloride	143	2.8	0.14	0.12
Nitrate	89[b]	1.0	1.0	0.88
Bicarbonate	296	2.4	0.008	0.007
Sulfate	84	0.6	0.0006[c]	0.005
Silicate	43	0.4		
Phosphate	25	0.2		
Sodium	124			
Potassium	12			
Ammonium	b			
Calcium	66			
Magnesium	19			

[a] Summary report on Advanced Waste Treatment, WP-20-AWTR-19. Fed. Water Poll. Control Admin., 1968, p. 46.

[b] Distribution of nitrogen between ammonium and nitrate varies; assumed to be all nitrate here.

[c] Assumes 0.5 M nitrate in organic phase.

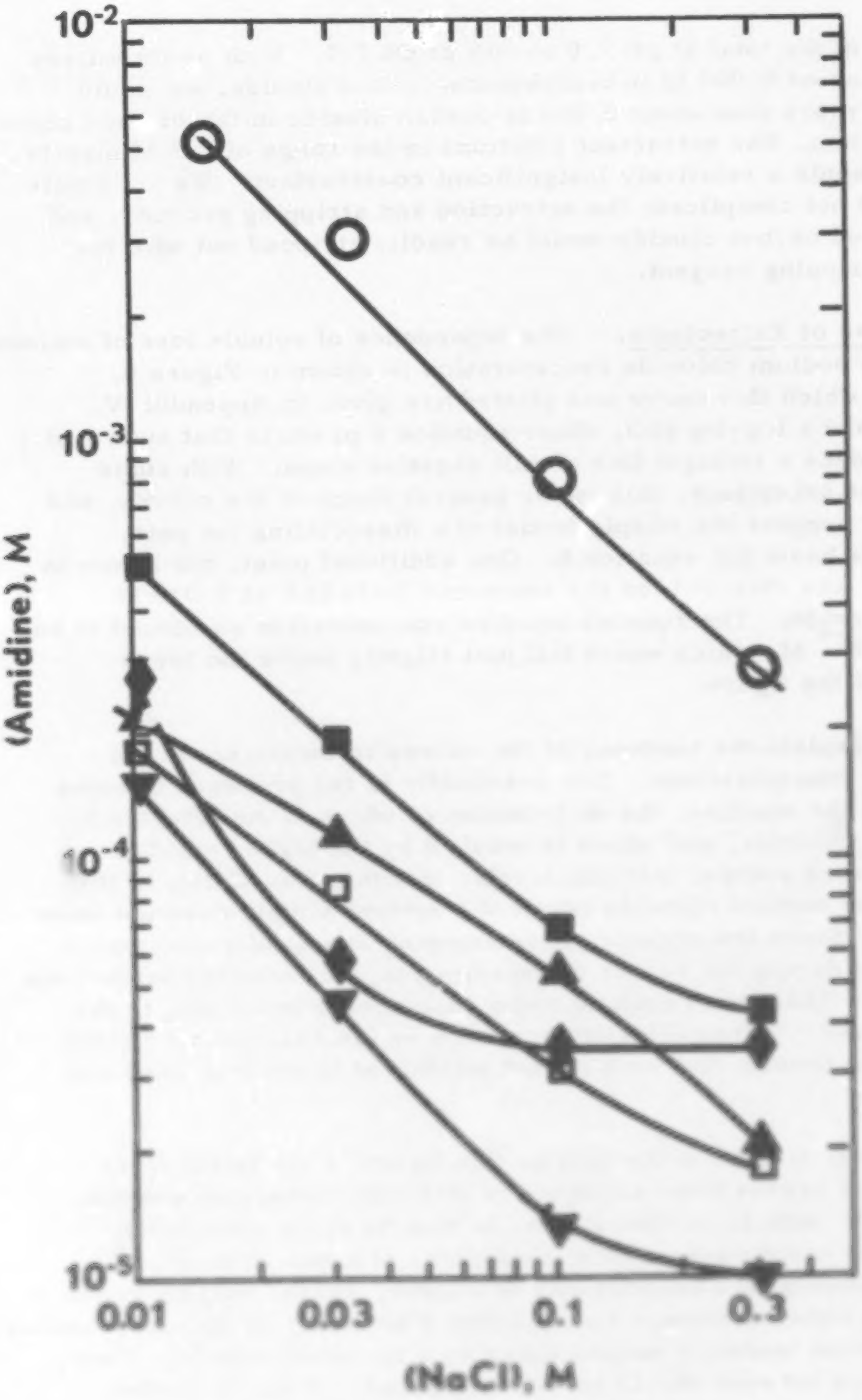


Figure 6. Soluble Loss of Amidines

Organic phase, 0.10 M hydrochloride salt of amidine.

○ Cy_2NoA in toluene
□ Eh_2EhA in toluene
■ Eh_2EhA in Chevron 3
▲ EhO-cEhA in Chevron 3
◆ Eh_2OcA in Chevron 3
▼ DoEhNdA in Chevron 3

about 70% of the total at pH 7.0 to 90% at pH 7.7. With waste waters averaging about 0.005 M in bicarbonate/carbon dioxide, we would not expect more than about 0.003 M carbon dioxide in the organic phase at equilibrium. For extractant solutions in the range of 0.5 M nitrate this represents a relatively insignificant coextractant. We anticipate this should not complicate the extraction and stripping process, and the absorbed carbon dioxide would be readily stripped out with the alkaline stripping reagent.

Soluble Loss of Extractants. The dependence of soluble loss of amidines on aqueous sodium chloride concentration is shown in Figure 6. Data from which this curve was plotted are given in Appendix IV. We have used a log-log plot, since equation 6 predicts that such a plot should produce a straight line of unit negative slope. With some conspicuous exceptions, this is the general shape of the curves, and the results support the simple model of a dissociating ion pair, which is the basis for equation 6. One additional point, not shown in the figure, was obtained for the compound DoEhEhA at 0.010 M sodium chloride. The aqueous amidine concentration was found to be about 8×10^{-6} M, which would fall just slightly below the lower boundary of the figure.

We cannot explain the tendency of the curves to flatten out at the higher salt concentrations. One possibility is the presence of some impurity in the amidine, the distribution of which is not affected by the sodium chloride, and which is masked by the higher amidine losses at lower sodium chloride levels. Another possibility is that at the higher sodium chloride levels the system simply does not obey equation 6. Since the organic phase remains essentially constant in composition during the series of experiments, any failures to obey the equation are likely the result of some phenomenon occurring in the aqueous phase. Either micelle formation or ion association effects might be the source, but we have not attempted to pin this down any further.

The important feature of the data in this figure is the fairly clear separation of curves from amidines of different molecular weights. The Cy$_2$NoA, with 21 carbon atoms, is clearly more soluble than any of the 24 carbon compounds, by factors of about 10 to 30. The cyclohexyl analog was actually run in toluene, which, judging by the comparison between toluene and Chevron 3 solutions of Eh$_2$EhA, lowers the distribution tendency toward water by a factor of about 2. Thus, the difference between the 21 carbon compound and the 24 carbon compounds is probably more nearly a factor of about 20 to 60.

An exception to this correlation is the compound DoEhNdA, which has 30 carbon atoms, but which is only slightly less soluble than the 24 carbon compounds. While this result may possibly be due to some experimental difficulty, we believe that it may very well be a real effect. We encountered a similar problem with the compound (Bu_2) EhEhA, the hydrochloride of which was not soluble to the extent of 0.1 M in Chevron 3. It was soluble in 0.010 M sodium chloride to the extent of about 0.04 M. We did not pursue this observation, but we are led to speculate that the rather high steric hindrance provided by the dibutylamine group may greatly reduce the ability of the hydrochloride salt to aggregate in the organic phase. If so, this would presumably increase the distribution tendency in the direction of the aqueous phase. The significance of this observation lies in the similarity of this compound to the compound DoEhNdA, which is also rather hindered as a result of the tertiary alpha carbon atom. This is clearly reflected in the relatively low apparent basicity, shown in Figure 1. Thus the relatively high tendency to distribute into the aqueous phase may also be a result of the high steric hindrance.

Some additional support for this hypothesis is to be found in the comparison between the curves for Eh_2EhA and EhOcEhA, where the latter compound is both less hindered and has a lower distribution tendency toward water.

The effect of concentration of amidine salt in the diluent on the soluble loss was determined for the compound Eh_2EhA, and the data are shown in Figure 7. The data show that little increase in soluble loss is observed with increasing extractant concentration above 0.1 M. Equation 16 predicts, for constant aqueous chloride concentration, a linear relationship between soluble loss and extractant concentration. However, the increase in aggregation of the organic salt with increasing concentration would be expected to stabilize the organic salt and reduce the tendency to distribute into the aqueous phase. This is, qualitatively, the observed effect.

The impact of soluble loss on the processing of a waste water occurs in two ways: as an economic problem, and as a pollution problem. The economic problem can be relatively easily estimated from the following equation:

Economic Cost (¢/M gal) = 0.83 x (soluble loss, mg/l) x (unit cost of compound, $/lb) (26)

Using a value of about $2 per pound of extractant (see next section) and the value of 8 x 10 M as the soluble loss of DoEhEhA (about 4 mg/l), the equation gives a cost of about 7¢/M gal due to soluble

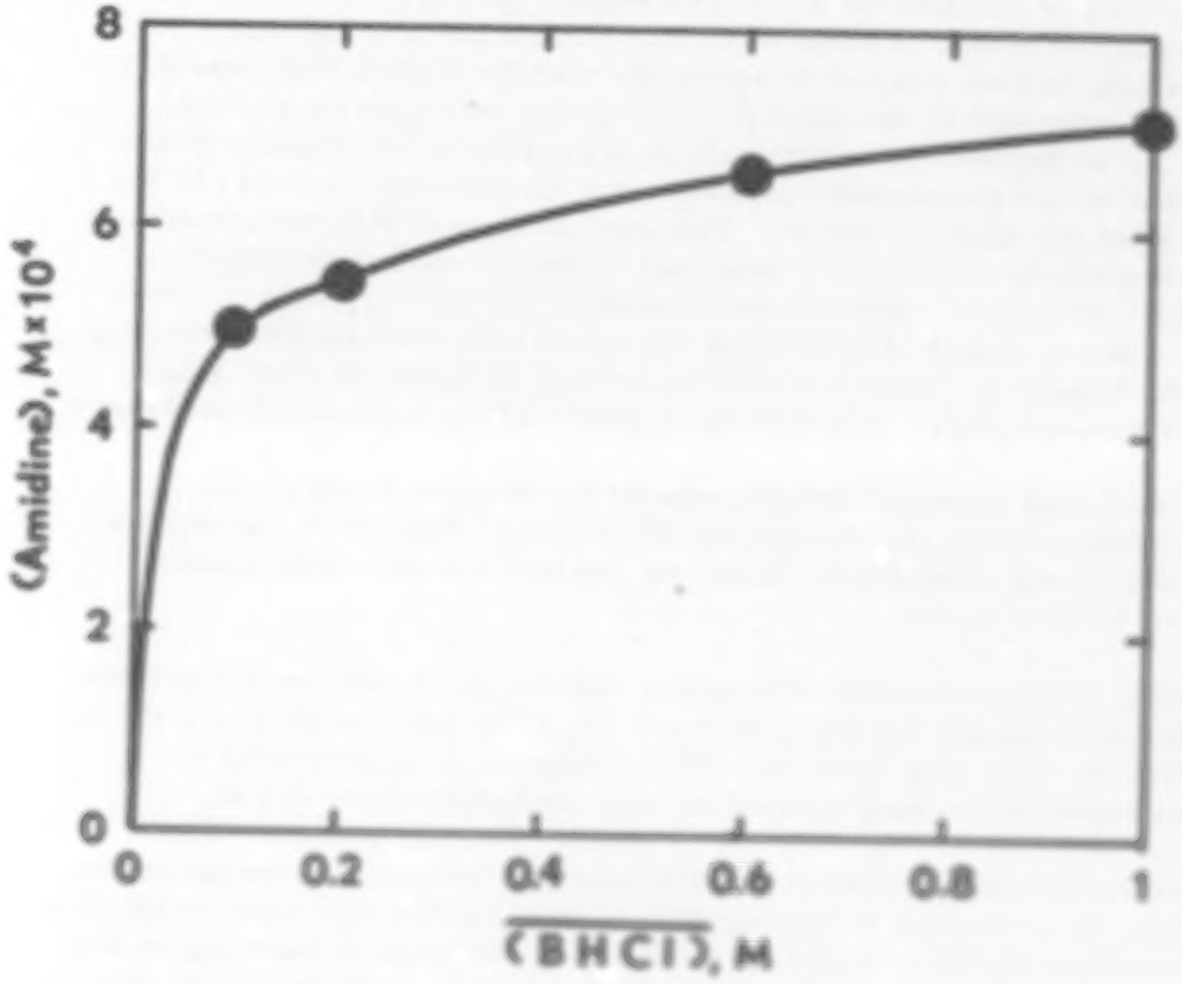


Figure 7. Soluble Loss of Eh_2EhA from Chevron 3 into 0.010 M NaCl

loss of extractant. This is a fairly high cost, and would very likely be unacceptable in most situations. However, this can be reduced fairly easily by switching to a higher molecular weight extractant. The data on soluble loss indicated that for each four carbons added to the extractant, a soluble loss reduction of something like 10-fold could be expected. Thus, the use of a second dodecyl group instead of a 2-ethylhexyl in the compound EhDoEhA should reduce the soluble loss to a level of about 0.1 mg/l. The cost of the compound would probably remain about the same, so that the economic loss represented by this value would be well below 0.2¢/M gal.

We have made no attempt to resolve the question of what is an adequately low concentration of an organic compound in a waste stream. One landmark of some use in considering the question is the fact that most secondary sewage effluents contain something of the order of 10-20 ppm of organic materials. While this can be further reduced with tertiary methods such as activated charcoal adsorption, there is no agreement that this is necessary for most situations.

Of more concern in this respect is the matter of biological activity. While preliminary biological activity tests indicated no highly significant activity, we did not examine biodegradability or toxicity to marine organisms. It is known that amidines hydrolyze to amides, and thence to carboxylic acids, producing also at each step an amine. Biological testing of all of these materials would probably be required in future development work.

Chemical Stability. Although this aspect of extractant characteristics was not defined as a separate property in the proposal, it is nevertheless an important feature of the extractant system. It is generally known that amidines are susceptible to hydrolysis to the corresponding amide, and this reaction represents at least a potential source of difficulty in the use of these materials. However, the stability experiments showed clearly that, in contact with either 0.1 M ammonium hydroxide or 0.1 M sodium hydroxide no observable hydrolysis occurred in eight months. The following calculation will show that hydrolysis should be a negligible factor in the operation of a water treatment process.

A reasonable flow rate of water through a resin bed is around 2 gpm/cu.ft., and if we assume the bed is on the treatment step of the cycle for only 50% of the time, then in eight months (the duration of the stability experiment) one cubic foot of resin will have treated about 400,000 gallons of water. If we assume 40% voids in the bed, 30-35 pore volume in the bead, and a 10% solution of extractant, a

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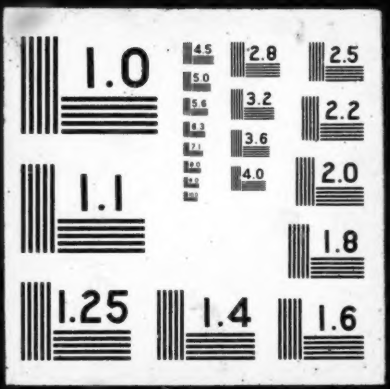
1.0
4.5
5.0
5.6
6.3
7.1
8.0
9.0
2.8
3.2
3.6
4.0
2.5
2.2
2.0
1.8
1.1
1.25
1.4
1.6

cubic foot of bed will contain about 6 lb. of extractant. Assuming also a degradation of about 1% (about the limit of detection) in the eight month experiment, the bed is found to have treated about 6.5 million gallons of water per pound of material degraded. At a cost of $2 per pound, the loss amounts of 0.03¢ per M gal of water. This is a negligible cost, but assumes the extractant can be used until complete degradation occurs. In practice the formation of the amide and amine might complicate the addition of new amidine to maintain the extractant strength, and a more realistic assumption might be that the system is discarded after about 10% degradation by washing it out of the beads with fresh diluent. This is equivalent to saying that only one-tenth as much water will be treated as in the above calculation, leading to a cost of about 0.3¢/M gal. Even this would be a relatively minor cost, and in terms of the above calculation, would require at least 10 x 8 months, or about seven years, to occur.

Soluble Loss of the Diluent. We have assumed that the extractant system absorbed into the polymer bead would consist of a solution of the extraction in a diluent. The main function of the diluent is to reduce the viscosity of the extractants, which in the salt form are extremely viscous liquids or waxy solids. It would be expected that diffusional processes would be relatively slow in such media, and the resultant column performance would be poor. Because of the desire to maintain soluble losses in the part-per-million range, the only classes of diluents which can be considered are the hydrocarbons, which are both relatively inexpensive and low in water solubility. While the aliphatic hydrocarbons are the least soluble, for a given molecular weight, they are also poorer solvents, and our experience with highly polar solutes like the amine salts, is that they are poorly soluble in the aliphatics, and in addition lead to higher solution viscosities. We have rather arbitrarily used a high-boiling aromatic hydrocarbon, Chevron 3, in most of the studies, since it combines rather well a high boiling point, high aromatic character, low cost, and relatively low solubility.

Some initial data on diluent solubility were obtained early in the study by contacting diluents with water, filtering the aqueous phase to clarify it, back extracting the water phase with carbon disulfide, and analyzing the latter solution with gas-liquid chromatography. Subsequent work has indicated that diluent is apparently lost from the aqueous phase during the filtration, either by absorption on the paper, or by evaporation. A subsequent experiment was carried out using only centrifugation as the method for clarifying the aqueous phase. The experiment involved successive contacts of Chevron 3 with 0.010 M sodium chloride. The GLC analysis technique was used, and was checked by another back extraction of the aqueous phase with loss of extractant. This is a fairly high cost, and would very likely be unacceptable in most situations. However, this can be reduced fairly easily by switching to a higher molecular weight extractant. The data on soluble loss indicated that for each four carbons added to the extractant, a soluble loss reduction of something like 30-fold could be expected. Thus, the use of a second dodecyl group instead of a 2-ethylhexyl in the compound EhDoEhA should reduce the soluble loss to a level of about 0.1 mg/l. The cost of the compound would probably remain about the same, so that the economic loss represented by this value would be well below 0.2¢/M gal.

We have made no attempt to resolve the question of what is an adequately low concentration of an organic compound in a waste stream. One landmark of some use in considering the question is the fact that most secondary sewage effluents contain something of the order of 10-20 ppm of organic materials. While this can be further reduced with tertiary methods such as activated charcoal adsorption, there is no agreement that this is necessary for most situations.

Of more concern in this respect is the matter of biological activity. While preliminary biological activity tests indicated no highly significant activity, we did not examine biodegradability or toxicity to marine organisms. It is known that amidines hydrolyze to amides, and thence to carboxylic acids, producing also at each step an amine. Biological testing of all of these materials would probably be required in future development work.

Chemical Stability. Although this aspect of extractant characteristics was not defined as a separate property in the proposal, it is nevertheless an important feature of the extractant system. It is generally known that amidines are susceptible to hydrolysis to the corresponding amide, and this reaction represents at least a potential source of difficulty in the use of these materials. However, the stability experiments showed clearly that, in contact with either 0.1 M ammonium hydroxide or 0.1 M sodium hydroxide no observable hydrolysis occurred in eight months. The following calculation will show that hydrolysis should be a negligible factor in the operation of a water treatment process.

A reasonable flow rate of water through a resin bed is around 2 gpm/cu. ft., and if we assume the bed is on the treatment step of the cycle for only 50% of the time, then in eight months (the duration of the stability experiment) one cubic foot of resin will have treated about 400,000 gallons of water. If we assume 40% voids in the bed, 30-35 pore volume in the bead, and a 50% solution of extractant, a cyclohexane, followed by determination of the ultraviolet absorbance of the aromatic content. The data are shown in Table IX. The sixth contact is considerably out of line, and we assume some contamination was involved. Both methods indicate the 5th and 7th contact to be in the same concentration range, although the UV figure is considerably higher than the GLC figure. We believe the explanation lies in the presence in the Chevron 3 of some nonhydrocarbon impurity. The GLC pattern showed four major components of the Chevron 3 in the standard solution. The back extracts, however, showed comparable amounts of an additional component, which was sufficiently delayed in the scan to indicate a different type of material. Such an observation could readily arise from slight oxidation of the hydrocarbon to an alcohol, phenol, ketone, etc. This type of compound would give a UV response similar to the hydrocarbon, but in this case was not included in the analysis in the GLC method. Because of the much greater water solubility of this type of an impurity, a significant response could be observed in the aqueous phase, even though the impurity is not detectable in the original hydrocarbon.

In the following section, data will be reported for resin column effluents, which agree reasonably well with the above data. Because of the ability of the GLC method to identify the hydrocarbon components, we believe it is a more reliable method for diluent loss determination, and the 21 ppm figure probably represents the diluent loss reasonably well.

Some further confirmation of this value can be obtained from examination of the boiling range of Chevron 3, which is given by the Standard Oil Co. as 182°C. to 205°C. This range contains the boiling points of most alkyl benzenes containing four aliphatic carbons in the substituent groups. Solubility data for some hydrocarbon material(48) indicate that such compounds should exhibit a water solubility in the range of 15-20 ppm, quite close to the observed GLC value. Since heavier diluents are available, it would probably be desirable to switch to such a material, possibly even to an aliphatic diluent, the soluble loss for which would be much lower still.

Water Extraction and Volume Change. The water extraction experiments were carried out mainly as an additional means of characterizing the organic extractant system. The data for water extraction by Eh_2EhA are shown in Figure 8, and show that there is a roughly linear correlation between amidine hydrochloride concentration and water concentration. The curves would intercept the y-axis at a concentration of about 0.03 M, which is approximately the solubility of water in toluene alone. Starting from this point, the slopes of the curves indicate that

Table IX

Comparison of Ultraviolet and GLC Analyses for Chevron 3 in Aqueous Phases

Aqueous Contact Number	ppm Chevron 3 UV	 GLC
5	36	21
6	78	100
7	29	21

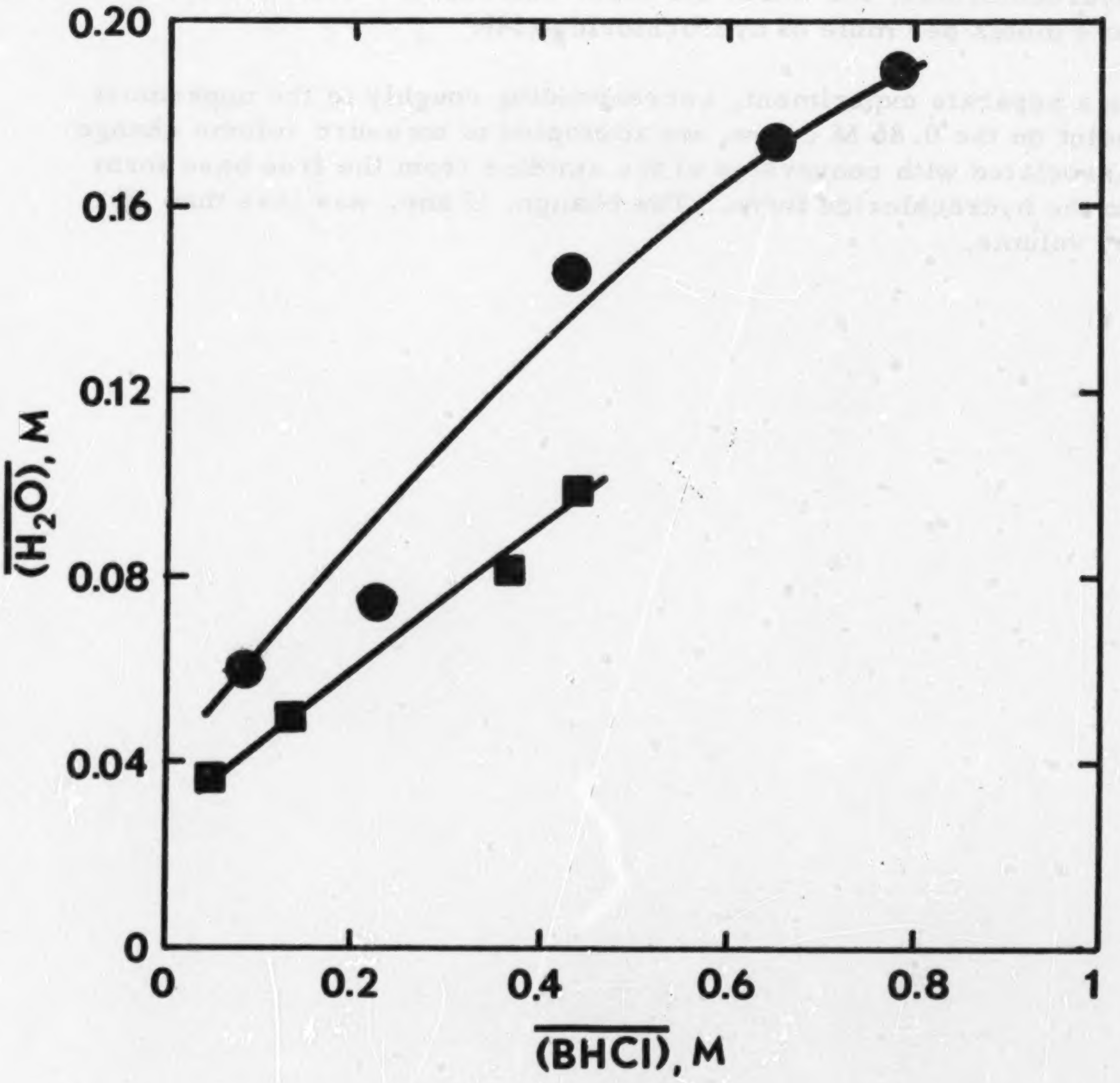

Figure 8. Extraction of Water by Eh_2EhA in Toluene.

Aqueous phase, 0.010 M NaCl

● $(\overline{B}) + \overline{(BHCl)} = 0.86$ M

■ $(\overline{B}) + \overline{(BHCl)} = 0.48$ M about 0.2 mole of water is taken up for every mole of amidine hydrochloride. This can be compared with earlier data on aliphatic amine hydrochlorides, for which the water extraction varied widely, from 0.05 to 4 moles per mole of hydrochloride (34).

In a separate experiment, corresponding roughly to the uppermost point on the 0.86 M curve, we attempted to measure volume change associated with conversion of the amidine from the free base form to the hydrochloride form. The change, if any, was less than 2% by volume.

ION EXCHANGE BEHAVIOR OF SOLID SUPPORTED EXTRACTANTS

A second aspect of this project involved a study of the feasibility of using amidine extractants absorbed in a macroporous copolymer to selectively remove nitrate from aqueous solutions. The extractant-in-bead approach was chosen because it minimizes two problems often associated with conventional liquid-liquid extraction processes; namely, the loss of extractant by physical entrainment and the formation of emulsions that coalesce slowly. The following discussion describes the incorporation of extractants into macroporous copolymers and their ion exchange behavior in packed columns.

Incorporation of Extractants into Macroporous Copolymers

Solid Absorbent. The solid absorbent used in this study as a support for the liquid extractant was a macroporous styrene-divinylbenzene copolymer resin that was obtained from the resin synthesis group of The Dow Chemical Company. This material is produced as an intermediate in the manufacture of macroporous ion exchange resins, however, it does not contain any ion exchange functionality. Similar macroporous copolymers are also available from the Rohm and Haas Company.

Macroporous resins differ from the more conventional gel resins in that they possess a true pore structure that is a significant fraction of the total resin volume. Gel resins, on the other hand, are essentially homogenous crosslinked copolymers that do not have any significant pore volume. Macroporous resins have been produced with total porosities as high as 50%, and with average pore diameters ranging from 50 to 1500 Å, depending on the particular polymerization procedure. Because the macroporous resins are highly crosslinked, they exhibit very little swelling in either aqueous or organic solvents. Consequently, their capacity to absorb organic extractants from an external solution is determined primarily by the pore volume that is accessible to the extractant. In contrast, the absorption capacity of a gel resin for an organic extractant depends almost entirely on the amount of resin swelling that is produced by the extractant solution. A macroporous resin was chosen for this study because it was found to have about a two-fold greater absorption capacity for the extractants of interest than did the gel resins. It was also felt that an extractant in a macroporous resin would exhibit better ion exchange kinetics than it would in a gel resin, although this point was not investigated.

The macroporous resin was supplied as spherical beads with a size range of 18 to 80 mesh, which were further screened and the 30 to 40 mesh fraction was used in all column experiments. The resin was washed with acetone and water to remove any residual monomers and vacuum dried at 60°C. The copolymer contained a nominal 20% divinylbenzene crosslinking which gave a rigid polymer bead. Total porosity of the resin was 26%, and 95% of the pores were less than 350Å in diameter.

Extractants. At the beginning of this project, the high molecular weight amidines were not available in large enough quantities to permit their use in resin experiments. Consequently, we used two other similar extractants that are commercially available to develop the resin loading procedure and to investigate some of the column operating parameters. The two substitute extractants were Amberlite LA-2, a secondary amine with an equivalent weight of 387, and Aliquat 336S, a quaternary ammonium chloride with an equivalent weight of 442. Neither of these two compounds meet all the criteria stated on page 9 for a suitable nitrate extractant. For example, Amberlite LA-2 is too weakly basic to be useful at the normal pH of natural waters, and Aliquat 336S cannot be stripped with alkali. Nevertheless, they are similar to the amidine extractants in many other respects and they served as useful substitutes for our initial investigations. When the amidine DoEhEhA became available in quantity later in the project, we used it exclusively in the resin studies.

Preparation and Properties of Extractant Loaded Resins. A standard procedure for incorporating liquid extractants into macroporous resins was developed. The extractant was dissolved in a high boiling aromatic hydrocarbon, Chevron 3, and two volumes of this solution were mixed with one volume of 30-40 mesh resin for at least 24 hours. The interstitial solution was removed by gentle suction filtration and the resin was rinsed several times with an aqueous solution of composition: 1 M NaCl, 0.04 M NaOH and 0.05% Triton X-100. The non-ionic surfactant, Triton X-100, was added to the rinse solution to facilitate removal of the surface adhering organic layer from the resin particles. The number of rinses was kept to a minimum, consistent with obtaining a relatively free-flowing resin while at the same time, maintaining maximum extractant absorption.

Only moderate success was obtained with this procedure in producing a truly free-flowing loaded resin. Generally, the loaded resins tended to form aggregates when placed in water because of the hydrophobic nature of the surface adhering organic layer. We anticipated that this behavior might impede optimum column performance due to the difficulty of obtaining close packing of the resin particles. It was found that a truly free-flowing loaded resin could be obtained if most of the Chevron 3 diluent was removed by evaporation; however, we were reluctant to employ this technique because we felt that the presence of the diluent in the resin was necessary to maintain a homogeneous solution of the extractant in the pores. Without a diluent, the extractant salts are very viscous materials and if any ion exchange could occur in the absence of a diluent, it would probably be extremely slow. We intended to investigate the ion exchange behavior of a diluent-free loaded resin, but time did not permit. Consequently, in all work reported here, the loaded resins contained both a diluent (Chevron 3) and an extractant.

Small (26), in his work on gel liquid extraction, reported that organic swollen gel beads did not aggregate when placed in water if the beads were previously surface sulfonated. The thin surface shell of sulfonated copolymer provided the bead with a hydrophilic surface that was easily wet by an external aqueous solution. We attempted to apply this same approach to eliminate the aggregation problems observed with the loaded macroporous resin. Several batches of macroporous copolymer were partially sulfonated with 96% H_2SO_4 at 90-100°C. Reaction times varied from 2-10 minutes, and the extent of sulfonation achieved varied from 0.5 to 7% of the maximum amount possible (about 5 meq./g.). These materials definitely showed less tendency to aggregate in water when loaded with an extractant, however, the extractant absorption capacity of even the least sulfonated resin was about 17% less than a comparable unsulfonated macroporous resin. Because of this rather significant reduction in absorption capacity, we waived further investigation of this approach in hopes that the aggregation of the unsulfonated resin would not adversely affect its column behavior.

Extractant Absorption Capacities. The amount of extractant absorbed by the macroporous copolymer was determined for each of the three extractants: Amberlite LA-2, Aliquat 336S, and DoEhEhA. Some typical results are shown in Table X. Throughout this report, the extractant loaded resins are designated with the following code: MP = macroporous, A = DoEhEhA, LA = Amberlite LA-2, Q = Aliquat 336S. Resins that differed only in the amount of extractant absorbed are distinguished by a number following the letter code.

Table X

Extractant Absorption Capacities of the Macroporous Copolymer

Resin	Extractant	Concentration of Extractant Solution (meq/ml)	Absorption Capacity meq. /g. Dry Resin[a]	Absorption Capacity meq. /g. Loaded Resin
MPA-1	DoEhEhA	0.971	0.887	0.424
MPA-2	DoEhEhA	0.560	0.354	0.151
MPLA	Amberlite LA-2	1.100	0.852	0.440
MPQ	Aliquat 336S	0.725	0.445	0.203

[a] Dry resin refers to copolymer beads only.

The extractant absorption capacities were determined by washing a weighed sample of loaded resin several times with acetone to remove the extractant, followed by potentiometric titration of the combined acetone washings. Amberlite LA-2 and DoEhEhA were determined with standard HCl and Aliquat 336S (chloride salt) with standard $AgNO_3$. The acetone-washed resin was vacuum dried and weighed.

It is evident from Table X that the amount of extractant absorbed by the macroporous copolymer increased as the concentration of the external extractant solution increased. Because of the high viscosity of concentrated extractant solutions, we arbitrarily chose 50% (about 1 N) as the maximum extractant concentration. Although more concentrated solutions would probably have given greater resin loadings, it was felt that the rate of ion exchange would be substantially reduced due to the high viscosity of the extractant solution in the resin pores. Since the aqueous phase does not permeate an organic loaded resin bead to any significant extent, ion exchange must occur primarily at the aqueous-organic interface on the bead surface. In the case of the DoEhEhA resins, this requires that amidinium chloride must diffuse from the interior of the bead to its surface and amidinium nitrate must diffuse in the opposite direction. A highly concentrated, and therefore highly viscous, DoEhEhA solution in the bead pores would restrict the rate of diffusion within the bead, which would result in a low rate of ion exchange. This argument would be true regardless of the nature of the diffusing species.

Column Studies

Experimental Procedure. Three of the four resins shown in Table X were investigated in the column experiments: MPA-1, MPA-2, and MPQ. Each of these materials was prepared using the 30-40 mesh copolymer. The column consisted of a 1/2" diameter by 23" high glass tube with adjustable bed support plungers on each end[3]. A dual syringe metering pump was used to pump solutions through the column at some predetermined flow rate from 2.4 to 10.4 ml/min. (1/2 to 2 gpm/ft^2). Effluent from the column was collected and analyzed, and breakthrough curves were constructed from these analyses. The composition of the feed solution was 0.001 M KNO_3 (62 mg. NO_3/l), 0.01 M NaCl(355 mg. Cl/l.) and pH 6.5

Packing the extractant loaded macroporous resins into the column presented some difficulties because of their tendency to aggregate and because they were less dense than water. The procedure that was adopted was to slurry a known weight of loaded resin with a 1N NaCl solution in the column. A long glass rod was worked up and down through the resin slurry to remove air bubbles, and the salt solution was allowed to slowly drain from the column. When the floating resin column began to accumulate against the lower bed support, it was lightly tamped in place with the glass rod, working from the bottom to the top of the column. The salt solution was never allowed to drain below the top of the resin bed. A final compression of the bed was accomplished by pressing the upper bed support plunger against the top of the resin bed. Bed heights ranged from 36 to 47 cm., and column volumes ranged from 45 to 60 ml.

After loading the column with MPA-1 and MPA-2, several bed volumes of 0.1 N HCl were pumped through the column to convert all the free-base DoEhEhA to the hydrochloride salt. The interstitial acid solution was then removed with several more bed volumes of 0.01 M NaCl until the effluent was neutral. Since the MPQ resin was already in the chloride form, it was preconditioned with 0.01 M NaCl only.

Analytical Methods. Nitrate in the column effluent was determined spectrophotometrically at 210 and 220 m μ (49) after extraction of interfering ultraviolet absorbers with spectroquality cyclohexane. A 5 ml. sample of effluent was shaken for several minutes with a like amount of cyclohexane and centrifuged. The absorbance of the aqueous phase was determined using 1.0 or 0.1 cm. quartz cells and a Cary 14 spectrophotometer. When necessary, the effluent solutions were diluted to give absorbance readings less than 1.0.

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[3] Available from Chromatronix, Inc., Berkeley, California

The molar absorbtivity for nitrate at 210 mµ was 8200; and at 220 m µ, 3750. The absorbance ratio, A_{210}/A_{220}, was consistently 2.18 ± 0.03. Any values that fell outside this range indicated the presence of ultraviolet absorbers other than nitrate, and required that the analysis be repeated.

In general, the cyclohexane extraction removed all interferences and the nitrate analyses were simple and rapid. One difficulty was encountered early in the work due to leaching of the plasticizer from the Tygon tubing used with the column. The plasticizer was not extracted by cyclohexane and it interfered with the nitrate absorbance. This problem was remedied by replacing the Tygon tubing with polyethylene and Teflon tubing.

Chloride was determined by coulometric titration using a silver anode. Chevron 3 was determined spectrophotometrically in the cyclohexane extract that was obtained from the nitrate analysis. Chevron 3 in cyclohexane showed a sharp absorption maximum at 222 mµ with an extinction coefficient of 0.0885 $l.\ mg.^{-1}\ cm^{-1}$.

DoEhEhA was determined by the picrate extraction procedure outlined in Appendix II.

Results of Column Studies

Nitrate breakthrough curves are shown in Figure 9 for three extractant loaded macroporous resins: MPQ, MPA-1 and MPA-2. The ratio of nitrate concentration in the column effluent to that in the feedwater, C_E/C_F, is plotted against the number of column volumes of feedwater treated. Each of these curves was obtained at a flow rate of 5.0 ml/min. The initial nitrate breakthrough from the MPQ resin occurred after only 30 column volumes of feedwater were treated, but nitrate extraction continued for more than 200 column volumes indicating a very slow rate of ion exchange for this resin.

The effect of flow rate on nitrate absorption was investigated using the MPA-2 resin and the results are shown in Figure 10. The breakthrough curves obtained at 2.4 and 5.0 ml/min. are nearly identical, and as expected, nitrate breakthrough occurred slightly later at 2.4 ml/min. than it did at 5.0 ml/min. Surprisingly, however, at 10.4 ml/min. the initial nitrate breakthrough occurred later and the amount of nitrate absorbed by the resin was larger than for either of the two lower flow rate runs. As the data in Table XI shows, about 66% of the extractant in MPA-2 was converted to the nitrate form at a flow rate of 10.4 ml/min; whereas, only 54% and 52% conversion

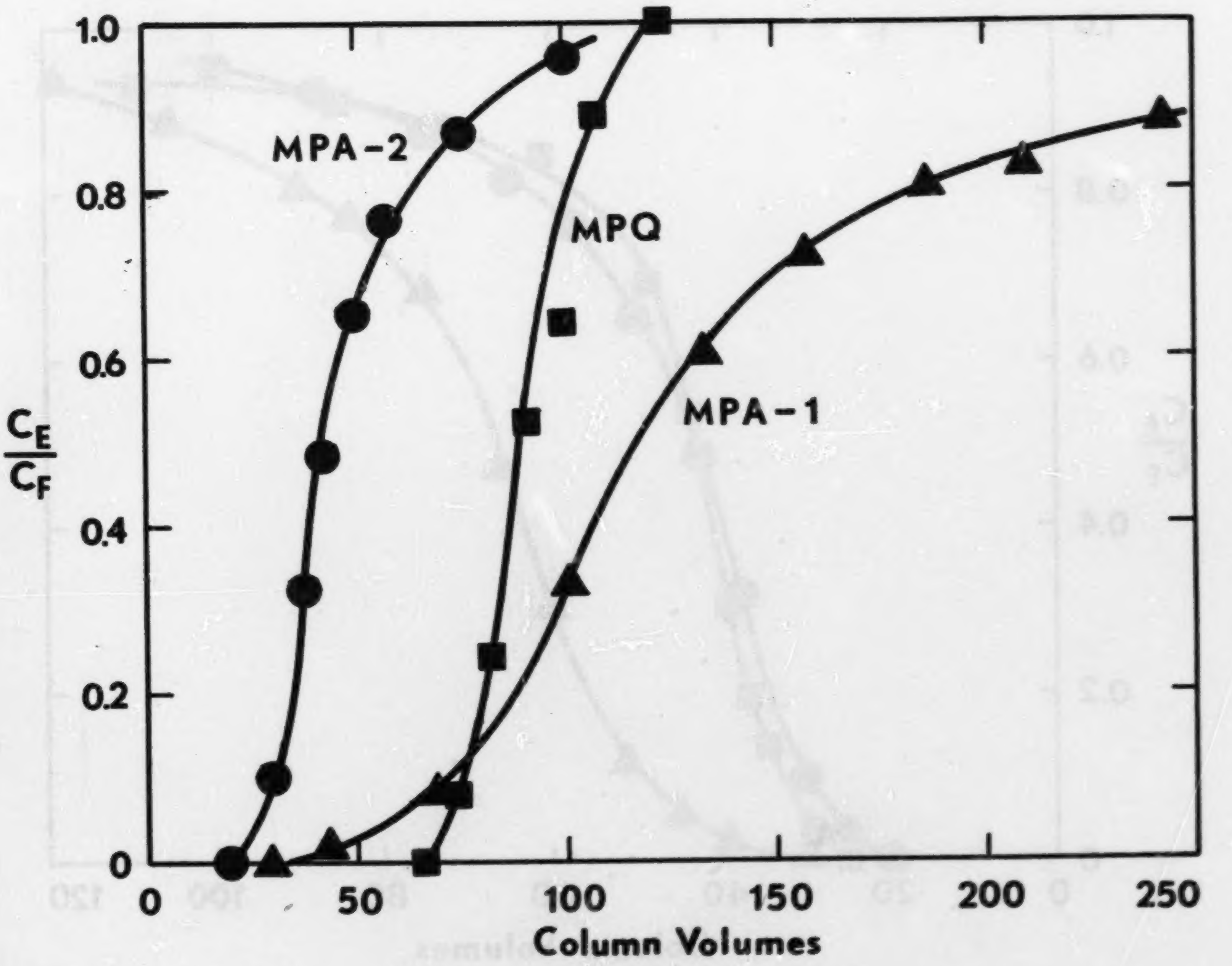


Figure 9. Nitrate Absorption by Extractant Loaded Macroporous Resins.
Feed Composition: 10^{-3} M KNO_3, 10^{-2} M NaCl
Flow Rates: 5.0 ml/min

● Column Volume = 60 ml; Capacity = 0.092 meq/ml
■ Column Volume = 45 ml; Capacity = 0.139 meq/ml
▲ Column Volume = 51 ml; Capacity = 0.252 meq/ml

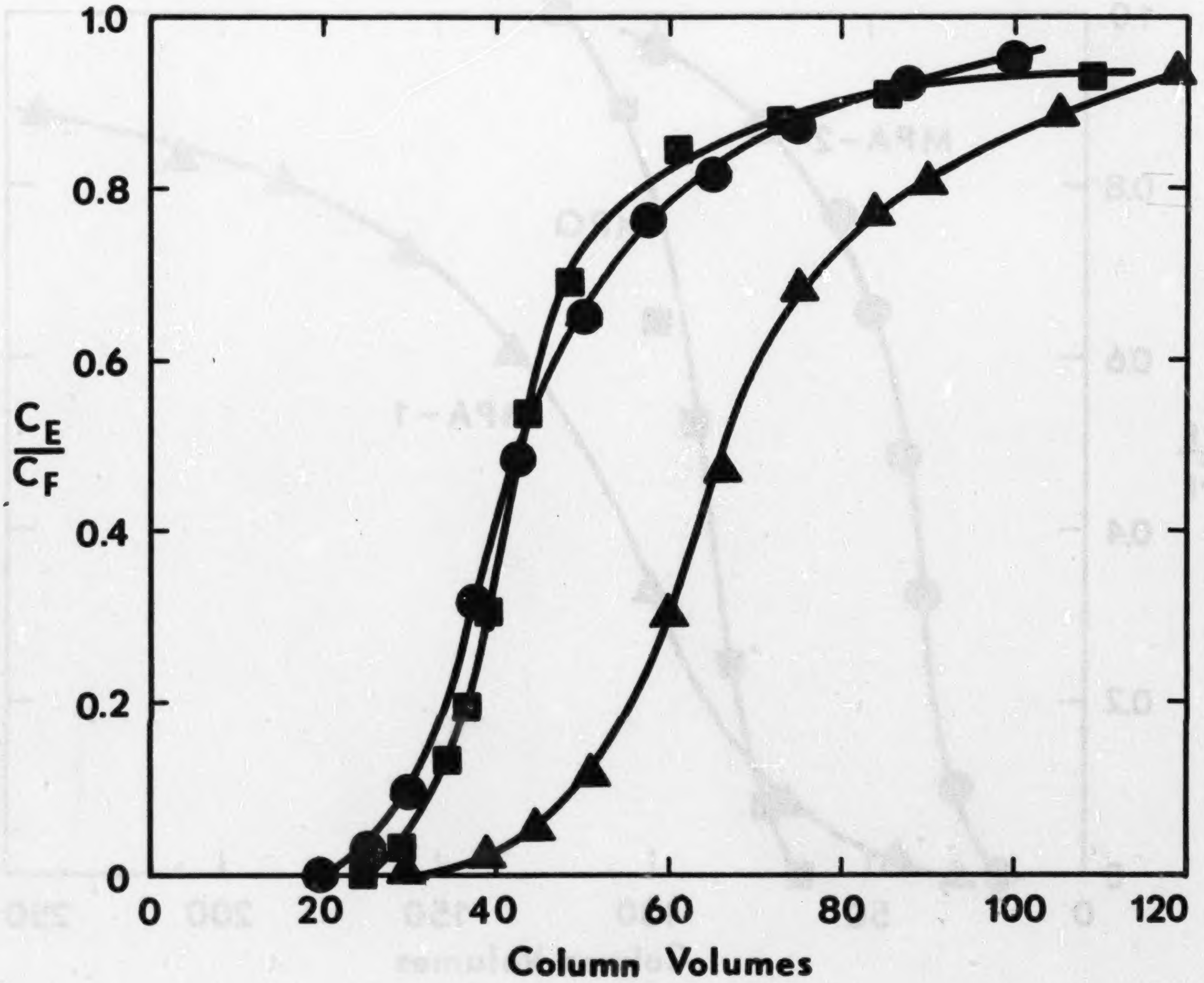


Figure 10. Effect of Flow Rate and Column Packing on Nitrate Absorption

Resin: 36.5 g MPA-2

Feed Composition: 10^{-3} M KNO_3, 10^{-2} M NaCl

■ Flow rate = 2.4 ml/min; Bed Volume = 60 ml
● Flow rate = 5.0 ml/min; Bed Volume = 60 ml
▲ Flow rate = 10.4 ml/min; Bed Volume = 52 ml

was obtained at 2.4 and 5.0 ml/min, respectively. The relatively low nitrate absorption at the lower flow rates was apparently due to severe channeling within the resin bed. All of the flow rate experiments with MPA-2 were done with the same sample of resin (36.5 g). Between each exhaustion cycle, the absorbed nitrate was eluted and the resin was regenerated with 0.1 N HCl. The amount of nitrate absorbed by the resin was calculated from a knowledge of the total nitrate applied to the column and the amount in the effluent after completion of an exhaustion cycle. During the exhaustion cycles carried out at 2.4 and 5.0 ml/min, the resin volume was 60 ml; whereas during the run at 10.4 ml, the resin volume was only 52 ml, a difference of 13%. This contraction of the resin bed was caused by the removal of air bubbles that had inadvertently accumulated in the upper third of the bed just prior to the high flow rate run. The air bubbles were removed by stirring the resin with a long glass rod, and when the resin bed was recompressed, its volume was only 52 ml. Since no resin was lost during this operation, the resin particles were more closely packed in the contracted bed than they were in the initial 60 ml bed. As a result, channeling was less severe during the high flow rate experiment and greater nitrate absorption was therefore obtained. These experiments indicate the importance of using a well packed resin bed to obtain optimum column performance.

Table XI

Nitrate Absorption Capacities of Macroporous Resins

Resin	Resin Vol. (ml)	Flow Rate (ml/min)	Extractant in Column (meq.)	Nitrate Absorbed (meq.)	Nitrate Absorbed (meq/meq) Extractant)	$S_{Cl}^{NO_3}$
MPQ	45	5.0	6.25	4.14	0.662	19.6
MPA-1	51	5.0	12.85	6.96	0.542	11.8
MPA-2	60	2.4	5.51	2.98	0.541	11.8
MPA-2	60	5.0	5.51	2.86	0.519	10.8
MPA-2	52	10.4	5.51	3.62	0.657	19.2

Selectivity coefficients, $S_{Cl}^{NO_3}$, were calculated for all resins investigated in the column studies and they are also given in Table XI. These coefficients were calculated by dividing the nitrate/chloride ratio on the resin by the nitrate/chloride ratio in the feed solution. Chloride on the resin was taken as the difference between the amount of extractant on the resin and the amount of nitrate absorbed. The nitrate selectivity of MPQ was 19.6, which agrees well with the values reported by Grinstead and Davis (33) for Aliquat 336S in a liquid-

liquid system. Likewise, the selectivity of 19.2 obtained for MPA-2 in the compacted bed is very near the average of the selectivities shown in Table V for DoEhEhA; again in a liquid-liquid system. Thus it was established that the nitrate selectivity of an extractant in a macroporous resin should be nearly identical to that in a liquid-liquid system. It is apparent from Table XI that the selectivities calculated for MPA-1 and for MPA-2 in the 60 ml. bed are considerably lower than would be expected for DoEhEhA in a liquid-liquid system. These low selectivities are undoubtedly the result of inefficient utilization of the resin due to poor column packing, and further emphasizes the necessity of preventing channeling within the column.

The loss of DoEhEhA from the resin during an exhaustion cycle ranged from 1.2 ppm at the beginning to 0.2 ppm at the end of the cycle. Chevron 3 losses ranged from a high of 40 ppm to a low of 10 ppm with an average loss of about 20 ppm. At this point the loss of diluent appears to present more of a problem than the loss of DoEhEhA.

Nitrate and chloride were eluted from exhausted DoEhEhA columns with aqueous NaOH and NH_4OH. Figure 11 shows the results of eluting MPA-2 (60 ml bed) with 0.5 N NaOH, and Figure 12 shows the corresponding results for MPA-2 (52 ml bed) using 0.5 N NH_4OH. In each case the alkali flow rate was 2.5 ml/min, and essentially all of the nitrate was removed with four column volumes of alkali. The data in Table XII indicates that reasonably good agreement was obtained between the amount of nitrate absorbed and the amount subsequently eluted. The elution curves illustrate that both NaOH and NH_4OH are equally effective reagents for nitrate elution from an exhausted column, however, the volume of eluate required to remove all the nitrate was larger than desired. The concentration of nitrate in four column volumes of eluate was only about 12.5 times that in the initial feedwater. Additional studies should be conducted to determine the conditions necessary to increase this concentration factor.

Table XII

Nitrate Elution from MPA-2 with NaOH and NH_4OH

Resin	Resin Volume (ml)	Reagent	Nitrate Absorbed (meq)	Nitrate Eluted (meq)
MPA-2	60	0.5 N NaOH	2.98	2.88
MPA-2	52	0.5 N NH_4OH	3.62	3.83

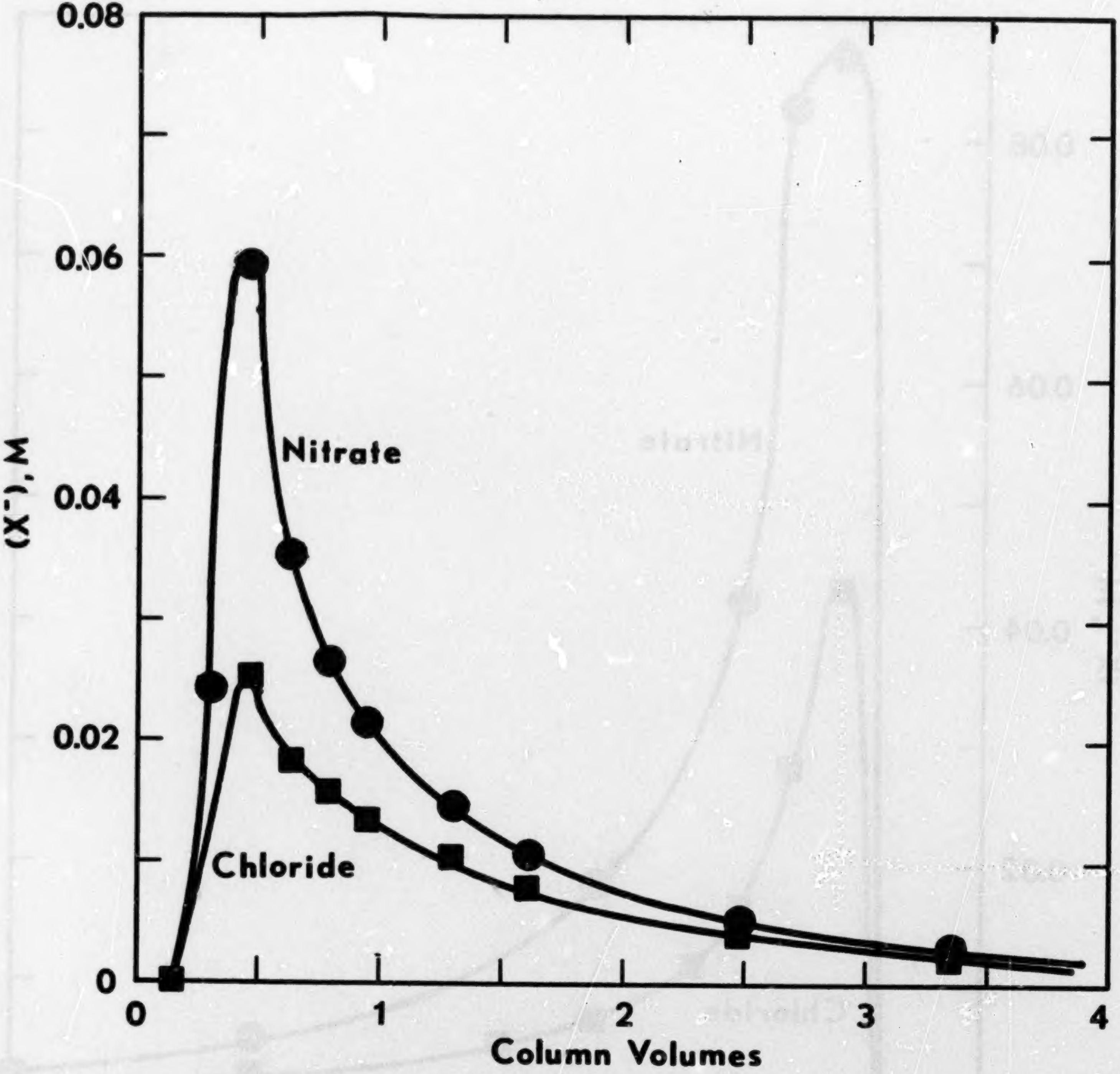


Figure 11. Nitrate and Chloride Elution with 0.5 N NaOH

Resin: MPA-2 (60 ml bed volume)

Flow rate: 2.5 ml/min

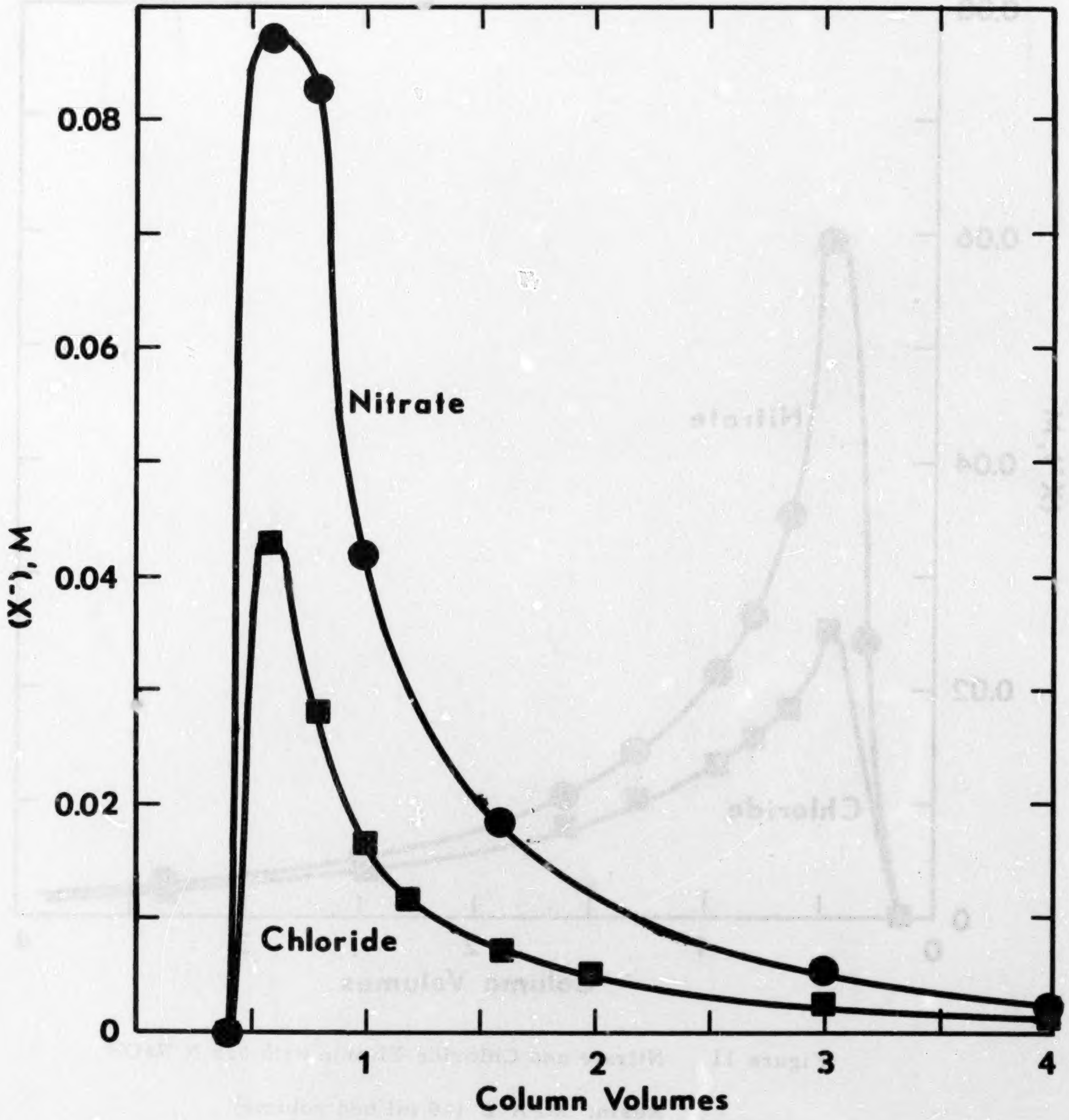


Figure 12. Nitrate and Chloride Elution with 0.5 N NH_4OH

Resin: MPA-2 (52 ml bed volume)

Flow rate: 2.5 ml/min

OUTLINE OF NITRATE REMOVAL PROCESS

Process Description

The goal of this study has been to examine a specific concept for a nitrate selective material which could ultimately be used in a practical process for waste water treatment. It is desirable, therefore, to attempt some evaluation of the potential of the concept at this stage.

The extractant-in-bead approach to nitrate removal has been based on eventual adaptation to a conventional fixed bed ion exchange process. This formed the basis of the earlier cost estimate for selective ion exchange (24). In its simplest form such a process would appear schematically as shown in Figure 13. A column of resin beads would be used to treat waste water until breakthrough of nitrate in the effluent occurred. This would be followed by a backwash, and an elution with an alkaline regenerant, which might be either aqueous ammonia or sodium hydroxide, to produce a nitrate solution. The column would finally be rinsed to eliminate contamination of the treated effluent from the following cycle by nitrate. The final eluate could be disposed of directly, if possible, or could be concentrated for disposal or use elsewhere.

Adaptation of Extractant-Loaded Beads to Column Operation

No specific criteria were set forth in the proposal for evaluating the success of the column operation of the extractant-in-bead system. However, one measure of the achievement is the degree to which column operations approached the conditions chosen for the preliminary cost estimates in the earlier Bureau of Reclamation contract. In that study the estimated cost of treating San Luis agricultural drainage water was about 6¢/M gal, without any credit for the proposed product, ammonium nitrate. In view of projected costs for other nitrate removal processes, this appears to be at least a competitive value. The major assumptions of that estimate regarding process variables were as follows:

1. feed water flow rate of 10 gpm/ft^2
2. nitrate loading of about 0.5 equivalents/liter of resin, obtained with a nitrate/chloride selectivity of 20, and a total resin capacity of 1.0 equiv./liter.
3. regeneration with ammonium hydroxide to give a 15% ammonium nitrate eluate.

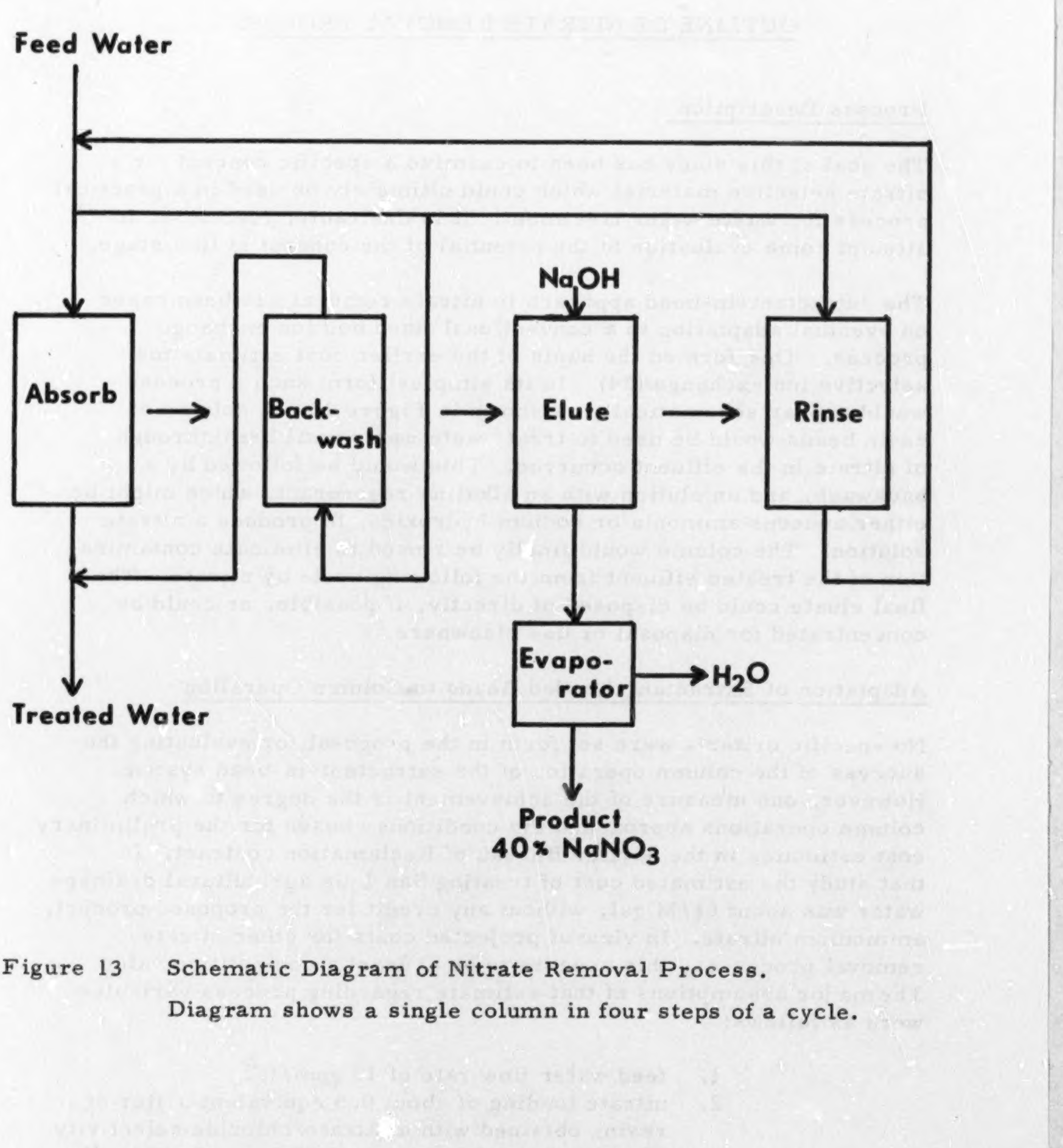

Feed Water
NaOH
Absorb
Back-wash
Elute
Rinse
Evapo-rator
H₂O
Treated Water
Product
40% NaNO₃

Figure 13 **Schematic Diagram of Nitrate Removal Process. Diagram shows a single column in four steps of a cycle.**

Because of the novelty of the system of liquid extractants in porous beads a number of problems had to be solved in order simply to reach the point of carrying out resin column experiments. For this reason, we have not been able to explore the desired range of process variables under items 1-3 above. However, we believe the column data do establish the technical feasibility of the system. Certain questions have had to be left unanswered, and the optimum form of the system, as well as the values of some of the parameters, are unknown at this point.

Flow Rate. The best column performance was the 10.4 ml/min. run shown in Fig. 10, which exhibited a nitrate selectivity of 19. The bed treated some 35 bed volumes of feed prior to detectable nitrate breakthrough, at a flow rate equivalent to 2 gpm/ft^2, and was apparently free from channeling problems. This resin consisted of batch MPA-2, which was made from the lower concentration of amidine solution, and the column contained only 5.5 meq of exchange capacity. The column prepared from a higher amidine concentration (MPA-1) actually contained over twice the capacity (12.85 meq), but was not operated at the 10.4 ml/min. flow rate. In order to estimate the operating capacity of a practical sized bed we shall first assume that the MPA-1 resin, if operated at the higher flow rate, would have treated at least twice the feed volume as did the MPA-2 resin, or about 70 bed volumes. We shall also assume that a reasonable estimate of scaled-up behavior can be obtained by comparing equal solution residence times. Thus, the 2 gpm/ft.^{2} run, which was done in a 16 inch deep bed, would be equivalent to a 10 gpm/ft.^{2} run in an 80 inch deep bed. While additional runs would be necessary to confirm this prediction, in particular runs with deeper beds and faster flows, we believe it is reasonable to expect that the 70 bed volume capacity could be achieved with the design flow rate of 10 gpm/ft^2.

Nitrate Loading. The original design value of nitrate loading was selected on the basis of capacities of conventional anion exchange resins, which commonly run somewhat greater than 1.0 milliequivalent/ml of bed (meq/ml). We have achieved values approaching 0.2 meq/ml, and this may well be about the upper limit in this type of system. The limitation is imposed by two factors: the fact that the absorbed extractant is mainly limited to the pore volume of the bead; and the presumed need for a diluent in order to maintain good diffusion. Pore volumes of macroporous beads currently available generally fall in the range of 30-40% of the bead volume. The highest extractant concentration in the absorbing solution has been about 1.1 M (about 50% by weight). Taking 33% and 1 M as the figures, and allowing a factor of 40% for interstitial volume in the bed (between beads), we calculate 0.2 meq/ml as a typical bed capacity.

While increases in bead porosity may be obtainable, we are not aware of any such materials. We have considered the possibility of eliminating the diluent, in order to increase the concentration of the extractant, and had planned to prepare and test a bed of such a material. The approach is an uncertain one, since this might immobilize the extractant, which is normally a viscous liquid or wax when in the salt form. In this case, probably only the extractant molecules adjacent to the aqueous interface would be effective. Practical utilization of the extractant molecules further inside of the bead would be prevented by the slowness of diffusion in a highly viscous medium. Such a limitation affects the column behavior in two ways. First, the lower bed capacity reduces the number of bed volumes of water which can be treated per cycle. Second, the concentration of nitrate in the eluate, for a given eluate volume, will be lower.

The importance of cycle length is that during at least a small portion of the cycle a resin bed must be undergoing regeneration and backwashing, during which time it is, of course, not treating feed water. The number of columns required in a particular installation is thus an inverse function of the fraction of the cycle devoted to absorption.

The cost estimate assumed a treatment capability of 374 bed volumes of water per cycle, with 90% of the time devoted to feed water. For a treatment capability of 70 bed volumes, only 70/374, or 19% as much time is devoted to feed water. If we assume the time devoted to regeneration is a constant, then the fraction of the cycle devoted to feed water is $\frac{0.19 \times 90}{0.19 \times 90 + 10}$, or about 63%. Thus, assuming other conditions to be the same, the current system would require 0.90/0.63, or 1.4 times as much cross sectional area in resin beds as was assumed in the estimate.

Elution Performance. The impact of the lower capacity on the eluate concentration is difficult to judge. We anticipated that the equilibrium between ammonia and the extractant system would be a measurable one, leading to tailing of the elution wave. Because of its greater base strength, no such effect is expected with sodium hydroxide. The observation of significant tails on both ammonium hydroxide and sodium hydroxide elution waves suggests therefore that elution is therefore limited by a kinetic process, and suggests that lower flow rates might reduce the tailing with either regenerant.

Other problems, such as mixing or channeling of flow in the bed, can also cause tailing, however. In fact, this problem is one of the major limitations on the ability to obtain high concentration eluates from an ion exchange bed. In the case of a bed with a total capacity of 0.2 meq/ml, for example, complete elution with a base should require just 0.2 meq. of base per ml of resin. In principle, this can be done with as little as 0.01 ml of 50% (~ 20 M) sodium hydroxide per ml or resin. However, this requires that a plug of 0.01 bed volume of solution be put into the column, and recovered undiluted. Because of the mixing at the leading and trailing edges of the plug, it would probably be necessary to collect considerably more volume, perhaps as much as 0.5 to 1 bed volume, in order to contain all of the plug of eluate. The achievable eluate concentration would be limited to 0.2 to 0.4 M, therefore. Thus, while the equilibrium should allow the nitrate to be completely removed from the resin, the difficulty of recovering the eluate without dilution severly limits the obtainable concentration.

Using the figure of 70 bed volumes of water treated per cycle, and a requirement of at least one-half of a bed volume of rinse water required each cycle, the greatest concentration factor possible between feed water and eluate is 70/0.5, or 140 fold. This would produce an approximately 0.14 M nitrate (about 1% $NaNO_3$) solution, containing chloride also, which would require evaporation or other means of concentration, in order to be utilized conveniently as a fertilizer material. With a 140 fold concentration factor into the eluate evaporation of a quantity of water roughly equivalent to 0.7% of the feed water would be required.

Some improvement in this situation could be realized by utilizing two resin beds in series, allowing one to be completely loaded before being switched off stream for elution. Inspection of the curves in Figures 9 and 10 indicates that at breakthrough, probably only one-third to one-half of the resin capacity has been utilized. Thus, two column operation, though somewhat more complex, could substantially increase the concentration factor between feed and eluate.

Handling of Beads and Other Operational Problems. Some other problems were encountered in the mechanical handling of the beads themselves, as was discussed earlier. In particular, the low density of the bead, which tended to make them float in water, and their hydrophobic character, which tended to make them clump together, complicated the preparation and operation of the resin columns. We are not certain how much difficulty these problems would create on a larger scale. No doubt some variations in the techniques of handling conventional ion exchange materials would be required.

Another problem arises from the slow disappearance of the extractant from the beads. Aside from the economic loss incurred, the beads can be expected to gradually lose their effectiveness, and some sort of procedure will be required to rejuvenate them or replace them.

Of course, if the frequency of this operation is low, its reflection in the economics of the process may not be significant.

In the system studied here we encountered losses of the extractant of the order of 1 ppm, and of the diluent of the order of 20 ppm. A cubic foot of polymer beads, loaded with a 50% solution of extractant, will contain about 6 lb. each of extractant and diluent. If we make the somewhat arbitrary assumption that a rejuvenation step would be required after 10% of one of the components has been lost, this would occur in this case after 0.6 lb. of diluent was lost, or after treatment of only about 3600 gallons of water per cubic foot of bed. If we further assume a five-foot deep bed treating 10 gpm/$ft.^2$, and the absorption step occupying 50% of the cycle, the 10% diluent loss would occur after only about 2 days of operation. As we pointed out earlier, switching to an appropriate higher molecular weight diluent would greatly reduce this loss. For a 1 ppm soluble loss of either component the 10% loss point would be reached in about 50 days. It is fairly certain, particularly in the case of the extractant, that soluble losses can be pushed down in the 0.1 ppm range. It is probably possible also for the diluent, but less data are available on this point.

The point which emerges from this discussion is that the major impact of small soluble losses of the reagents may not be the economic loss incurred, but rather the increase in complexity which results.

Several ways of managing the rejuvenation problem can be imagined. The simplest, operationally, would be that of using systems whose losses could be kept in the 0.1 ppm range or below, eliminating the need for frequent attention. Another method is simply to add the corresponding amount of material into the feed water, so that no change in the bed occurs at all. Still another approach is to utilize a bed of "empty", or extractant-free beads as a cleanup bed on the downstream side of the processing beds. This bed would pick up the soluble loss of extractant and diluent, and at some point, after absorption of a substantial amount of the extractant system, could be switched to the upstream side to act as one of the processing beds. At this stage of development, we believe that the most practical means of handling the problem lies in selecting compounds of extremely low soluble loss. To this end the use of a less soluble diluent, possibly even an aliphatic hydrocarbon, may be indicated. For the extractant, a somewhat heavier material than the DoEhEhA is indicated. The compound Do_2EhA (which we have not prepared) would probably be adequate. Besides a greatly reduced soluble loss, the compound should exhibit a slightly higher pK_a, which would also be desirable. Based on these modifications in the extractant system, rejuvenation can probably be handled adequately by a continuous addition to the feed water, as described above. If not, periodic, but presumably infrequent, soaking of the beads in a fresh extractant solution, either in place or in a separate tank, would probably be required.

As a final observation, we believe it is important to point out that the amidine extractants have a potential for application beyond their use in polymer bead absorbent systems. We believe that, based on the data obtained in this study, the amidines are suitable in every major respect for application to the problem of nitrate removal. The precise optimization of the structure has not been done, but we believe that synthesis of one or two additional compounds would be adequate, since predictions of the relevant properties of these materials can be made.

The major problems have been encountered, not with the compounds themselves, but with the means for employing them; that is, the contacting operation. Further development of the extractant-in-bead concept is obviously required, if this means of contacting is to be successful. However, other means may be available. One obvious type of operation is conventional liquid-liquid extraction. We expect that the major difficulty with an extraction approach would be the problem of reducing physically entrained extractant in the treated water to the part-per-million level. Certain advantages would become available in return, however, principal of which is the absence of any limit on the final eluate concentration. Thus, relatively concentrated nitrate eluates could be obtained with little difficulty.

Other more speculative methods for applying the selective amidine systems to nitrate removal also exist, but are beyond the scope of this discussion.

Commercial Availability of Amidines.

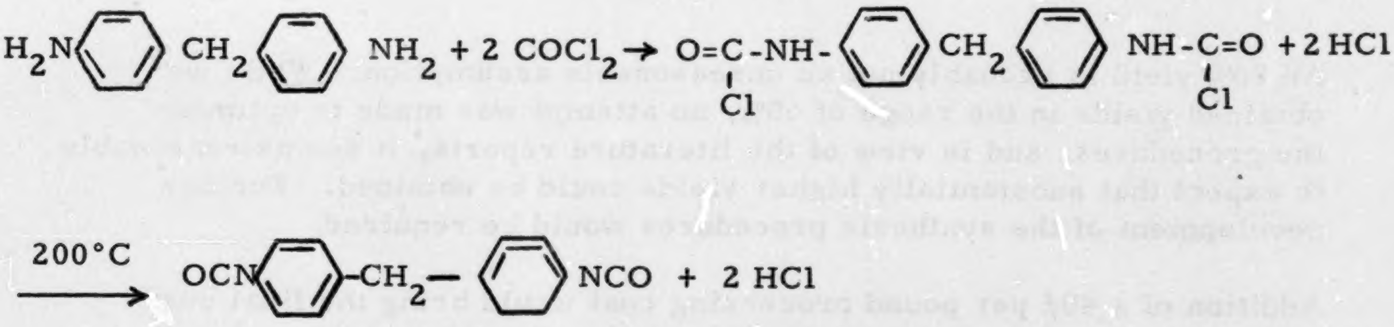
Except possibly for the lowest members of the amidine class, none is available as commercial materials. Any utilization of these compounds in a process such as was studied in this project would require development and synthesis of the desired compound for this purpose alone. The cost of a material under these conditions would depend not only on the raw material and processing complexity, but also on the scale of manufacture. For these reasons, prediction of the likely price of such a material is extremely difficult. Nevertheless, it is possible to make some estimates of the order of magnitude of cost of the final product. The following discussion is directed toward the compound DoEhEhA, which was the most promising of the materials included in this study. However, since a variety of both amines and carboxylic acids are available at comparable costs, compounds of other structure and of other molecular weights could readily be made at about the same price.

Carboxamides are available from a number of companies processing fatty acids. They are usually the simple unsubstituted amides, $RCONH_2$, and are prepared simply by heating the ammonium salt of the acid to dehydrate it. While the acids themselves (e.g. stearic acid, oleic acid) sell for 25-30¢/lb. the amides are quoted in the range of 50¢/lb. Since the ammonia represents such a small portion of the final product weight, and yields are probably close to theoretical, the only significant raw material cost is that of the acid. The remaining 20-30¢/lb. is attributable to the operating costs of the process. The scale of production is not known.

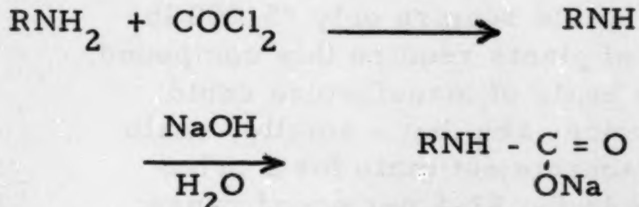
A somewhat more useful situation is represented by the synthesis of N, N-dibutyl-oleamide (DBO), which was studied on a pilot plant scale, using a simple dehydration process (50). Yields of the crude material ran about 95%. Using 53¢ and 23¢ per lb., respectively, as the costs of the amine and acid, estimated costs for the product amide were given as about 40c/lb. for production levels in the 2 to 10 million lb. per year range. Allowing about 35¢ per lb. for raw materials, the processing cost turns out to be only something like 5¢ per lb. The difference between this figure and the 20¢ estimated above for fatty amides is very likely connected with a difference in production scale.

The amide intermediate for the compound DoEhEhA would be prepared in a similar manner from 2-ethylhexoic acid and 2-ethylhexylamine. These two materials are quoted by Union Carbide Chemicals Corporation at 32¢ and 55¢ per lb., respectively. Since the amide is composed of about equal weights of acid and amine the raw materials cost of the amide is roughly the average of the two costs, or about 45¢ per lb. Using the estimates of processing cost discussed above and allowing for a 90% yield, the total cost of the amide intermediate, N-(2-ethylhexyl)-2-ethylhexamide, would probably fall in the range of 50-70¢/lb.

A model for the phosgene reaction step is more difficult to find. Phosgene is used, however, on a relatively large scale. One major use is in the production of diisocyanates, which are intermediates in the manufacture of polyurethane plastics. Another use is in the production of carbamate pesticides. Typical reactions are the following:



methylene dianiline diisocyanate (MDI)



$$RNH_2 + COCl_2 \longrightarrow RNH-\underset{Cl}{C}=O + HCl$$

$$\xrightarrow[H_2O]{NaOH} RNH-\underset{ONa}{C}=O$$

sodium N-alkyl carbamate

Economics on carbamate compounds are not plentiful. Information on diisocyanates is somewhat more accessible; the MDI shown above sells for about $1 per lb., and is manufactured on a scale of about 5 million pounds per year. Using known costs for methylenedianiline and phosgene of about 60¢/lb. and 15¢/lb., respectively, the raw materials costs for MDI at 90% yield would run about 60¢/lb. Processing and other costs for this reaction, therefore, amount to something like 40¢/lb of product.

Synthesis of an alkylated amidine according to the methods utilized in this study would be similar to the isocyanate synthesis. There is in each case an initial reaction with phosgene, followed by a second reaction involving an amine, in the amidine synthesis, or heat, in the isocyanate synthesis. The raw materials costs would appear as shown in Table XIII.

Table XIII

Raw Materials Costs for Amidine Synthesis

Compound	Unit Cost, ¢/Lb.	Theoretical Requirement, Lb. /Lb. Amidine	Raw Material Cost, ¢/Lb. Amidine
Amide	70	0.60	42
Phosgene	15	0.24	4
Dodecylamine	50	0.44	22
Total			68¢ (100% Yield) 85¢ (80% Yield)

An 80% yield is probably not an unreasonable assumption. While we obtained yields in the range of 60%, no attempt was made to optimize the procedures, and in view of the literature reports, it seems reasonable to expect that substantially higher yields could be obtained. Further development of the synthesis procedures would be required.

Addition of a 40¢ per pound processing cost would bring the final cost of the amidine up to about $1.25 per pound. This is probably a lower limit, since consumption of the amidines would presumably be relatively low. A 100 million gallon/day waste treatment plant, for example, losing 0.3 ppm of compound, would require only 75,000 lb per year as makeup. Should a number of plants require this compound, or if some other use were to arise, the scale of manufacture could result in a price in this range. The chances are that a smaller scale synthesis would be required, and a reasonable estimate for a price for this amidine is probably somewhere in the $2-5 per pound range.

Cost Projections

Preparation of a conventional cost estimate of the proposed process at this relatively early stage of development would be premature. We have achieved, however, some of the characteristics which were used as assumptions in preparing the earlier cost estimate for the Bureau of Reclamation contract (24). With suitable changes in that estimate it is thus possible to develop an approximate projection of processing costs for the extractant-in-bead process.

In Table XIV we give the basic assumptions which underlay the earlier cost estimate, which pertained to a hypothetical resin with a total capacity of 1.0 meq/ml, and a nitrate/chloride selectivity of 20. The estimate was based on treating 100 million gallons/day of agricultural drainage. We also show the corresponding assumptions involved in treating the same volume of municipal sewage with the extractant-in-bead system. We have made reasonable assumptions for costs of materials and processing capabilities, based on the above discussion. The major unproven assumptions involve a soluble loss of extractant of 0.3 ppm; a soluble loss of diluent of 1 ppm, and an eluate concentration of about 1% sodium nitrate. While unproven, they represent situations which can probably be realized with suitable and straightforward changes in the process as it now stands.

Table XV contains the projection of costs. The lefthand column summarizes the costs developed in the Bureau of Reclamation estimate, while the projections for the extractant-in-bead process are shown on the right.

Elimination of the ammonia and HCl costs results from the elimination of a somewhat involved purification process assumed in the earlier estimate. No change was made in the power or labor costs. Steam costs were increased by the same ratio as the increase in water evaporation requirements.

Capital costs were increased by the factor 1.4, which represents the estimated increase in number of ion exchange columns due to the lower fraction of cycle devoted to feed water. The resulting total processing cost, 16¢/M gal, represents an order of magnitude projection for this process, based on current capabilities.

From this projection it is possible to observe the character of the major processing problems. The single most important one, of course, is the high evaporation cost required by the relatively dilute eluate anticipated. Attempts to reduce this cost can proceed in a number of directions. One possibility is to increase the exchange capacity of the beads. However, due to the nature of the beads and the extractant system, it is unlikely this can be raised greatly; complete elimination of the diluent, for example, would only raise the capacity by a factor of 2. More promising approaches lie in the manipulation of the operating variables. Further work may determine that a smaller eluate volume will suffice. The 0.5 bed volume assumed here may be reduced by slower flow rates, or by recycling some of the more dilute portions of the elution tail back through the feed water. The use of a two column processing arrangement would probably be desirable, both in increasing the volume of feed water per cycle, and raising the ratio of nitrate to chloride in the loaded bed.

A secondary reduction in the projected cost can probably be anticipated in the extractant item. While we assumed a loss of 0.3 ppm, it is probably reasonable to expect an even lower figure. Thus, with proper choice of extractant, a significant portion of the 2¢/M gal might be eliminated.

Table XIV

Basis for Cost Projection

	Prelim. Cost Estimate, Bureau of Reclam. Contract	Proposed for Sewage Treatment
Plant Size, gal/day	100×10^6	100×10^6
Area Flow Rate, gpm/ft^2	10	10
Feed Water Composition, mg/l		
NO_3^-	90	62
Cl^-	1000	355
% of Cycle Time on Absorption	90	63
Bed Vols. Feed Treatment per Cycle	374	70
Resin		
Total Capacity, equiv/l bed	1.0	
Selectivity, NO_3^-/Cl^-	20	20
Cost, \$/cu. ft. (resin)	50	25
(contained extractant)		12
Resin Bead Life, Years	5	10
Extractant Loss, mg/l	-	0.3
" Cost, \$/lb	-	2.00
Diluent Loss, mg/l		1
" Cost, \$/lb		0.03
Elution		
Agent	25% NH_3 (aqueous)	~20% NaOH
Eluate Concentration	15% NH_4NO_3 1% NH_4Cl	~1% $NaNO_3$
Final Evaporated Product Conc.	54% NH_4NO_3 4 % NH_4Cl	40% $NaNO_3$
Lb. H_2O Evap'd/Mgal Treated Water	4	100

Table XV

Cost Projection

		Estimate of Bureau of Reclamation Contract		Preliminary Cost Projection for Sewage
Capital Cost				
Direct Fixed		$4,230,000		
Resin		2,826,000		
Total		$7,056,000		
Operating Costs			Costs, ¢/Mgal	
Raw Materials		4.51		3.8
NH_3	0.79		-	
NaOH	1.19		1.5	
HCl	1.48		-	
Resin Replac.	1.05		0.3	
Extract. "	-		2.0	
Diluent "			0.03	
Utilities		0.57		10.2
Power	0.16		0.16	
Steam	0.41		10	
Operating Labor		0.50		0.50
Capital Costs*		0.85		1.2
Total		6.4		15.7
Credit - NH_4NO_3 Sale		3.0		-
Net Cost		3.4		15.7

*Based on an amortization rate of 3.1%/yr.

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APPENDIX I
SYNTHESIS PROCEDURES

N, N'-Dicyclohexyl octanamidine Carbodiimide Method.

The Grignard reagent was prepared in 300 ml. ether from 100 g. (0.52 moles) of 1-bromo-octane and 12.6 g (0.52 moles) of magnesium in the usual manner. The solution was transferred to a dropping funnel and added dropwise to a dry solution of 71 g. (0.34 moles) of dry dicyclohexylcarbodiimide in another 300 ml of ether. The carbodiimide had been previously melted and filtered through sintered glass to free it of a higher melting impurity which was found in our samples.

After 24 hours water was added slowly with the flask packed in ice, then aqueous HCl was added until all the solid had dissolved. After separation of the aqueous phase, the organic (2 phases) was evaporated under reduced pressure. The residue had a very high KOH equivalent weight, indicating a neutral impurity which was removed by shaking with a large volume of pentane. A solid resulted, which was collected by suction filtration. The solid was a mixed bromide-chloride salt, so was shaken with pentane and 10% NaOH to convert to free base in pentane solution (some toluene added to help the solubility). The organic solution was filtered to remove entrained water, and anhydrous HCl bubbled through it. The hydrochloride split out as a liquid phase, and solidified only after all solvent, including water, which was probably responsible for its not crystallizing out of solution had been removed under reduced pressure. Yield: 50%.

N-(2-Ethylhexyl)-2-ethylhexanamide

105 g (.65 moles) of 2-ethylhexanoylchloride and 180 g. (1.39 moles) of 2-ethylhexylamine were each dissolved in 200 ml of ether and the amine solution was added slowly to the acid chloride solution with stirring. An ice bath helped control the copious fuming as well as termperature. Stirring was continued without the ice bath for approximately one hour after the addition was completed. The solution was then shaken with excess HCl(1). Water was added to effect a two-phase system and the mixture shaken again. Another acidified water wash was followed by two water washes, and the ether solution(2) filtered and evaporated under reduced pressure to a constant weight. Yield 92-4%.

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Notes:

1. Needed only for the amount of starting amine greater than twice the amount of starting acid chloride.

2. Aqueous washes were clear, and ether phase cloudy throughout.

N, N'-Di(2-ethylhexyl)-2-ethylhexanamidine. PCl_5 Method.

133 g (0. 64 moles) of PCl_5 was added to 163. 3 g (0. 64 moles) of 2-ethylhexyl-2-ethylexanamidine with mechanical stirring. The mixture was heated to 120° externally (95° internally) for 3 hours. 51 g. (0. 64 moles) of pyridine was added, then 83 g (0. 64 moles) of 2-ethylhexylamine, slowly, with the temperature maintained at 160° externally for 75 minutes longer. The heating was discontinued, and when the temperature had dropped to below 100°, 42 g of water was added slowly. Chloroform was added when the temperature had dropped below its boiling point, the aqueous separated, and the organic washed 3 times with water at 45° -60°C. The organic was evaporated under reduced pressure. The remaining oil was partitioned between 600 ml of 75% aqueous ethanol and 300 ml of pentane, and the ethanol solution washed 3 times more with 300 ml portions of pentane. On evaporation, an equivalent weight determination showed the product contained 18% neutral impurity. It was therefore converted to free base by shaking with 300 ml pentante and 10% NaOH, and washing the pentane solution 3 times with 75% ethanol. Evaporation of the pentane solution, with the temperature kept below 30° yielded the free base in 22% yield. HCl eq. wt. :391, calculated:367.

Prep. of N-Dodecyl-N'-(2-ethylhexyl)-2-ethylhexanamidine (DoEhEhA).

Phosgene Method.

Procedure: 46 ml (0. 65 moles) of phosgene was collected and dissolved in 200 ml of chilled toluene, then transferred to a dropping funnel. The solution was added to a solution of 78 (. 31 moles) 2-ethylhexyl-2-ethylhexanamide in 200 ml of toluene, in an ice bath. The rate of addition was such that the temperature stayed below 30°. The system was stirred overnight, after which excess phosgene was removed by a partial evaporation in vacuo. 57 g (0. 31 moles) of dodecylamine was dissolved in toluene and added dropwise to the reaction mixture, keeping the temperature ~ 30°. (A solid or 2nd phase split out). The system was stirred over a weekend[2].

An excess of HCl was added[3] and the mixture transferred to a separate funnel and washed 3 times with boiling water[4].

The final organic solution - still very cloudy - was gravity filtered through several paper filters,[5] and evaporated in vacuo[6] to a constant weight in a water bath at 80-90°C.

The material was dissolved in ~4 ml/gm of 80% ethanol (by volume - hereafter called ethanol solution) and shaken with ~half that volume of hexane three times. The ethanol solution was then evaporated in vacuo as the toluene solution was above.

Eq. wt (Cl^-):480, theo: 459 Yield: 60% based on 96% purity

Footnotes to DoEhEhA Prep:

1. Progress of this reaction was followed by samples periodically withdrawn and evaporated by blowing N_2 over them to evaporate the solvent and phosgene. An I. R. scan of the residue showed the relative strengths of bands at 5.9 μ (desired) and 6.1 μ (starting material) and incidentally at 5.7 (undesired).

2. Time necessary undetermined - all runs went overnight at this point, and the ones with best yields went 2 or 3 days due to weekends or holidays.

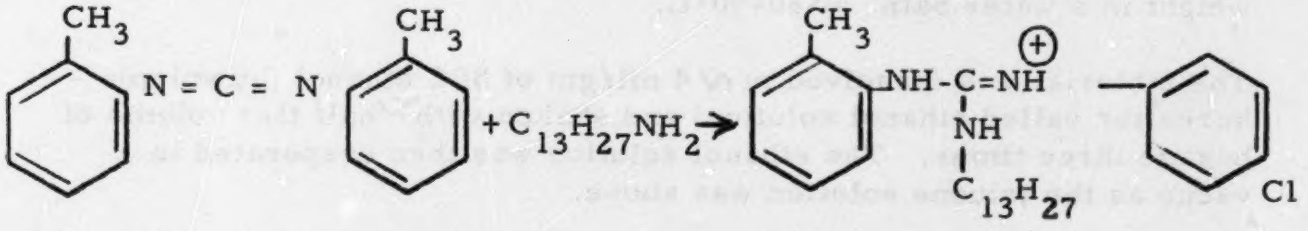
3. To convert excess amine to hydrochloride salt which is soluble in warm water.

4. The high temp. aids this slow separation - it is advisable to keep it hot (70°-80°) during the separation of phases.

5. This material can be tested for purity by converting a weighed sample to the free base by shaking with dil. aq. NaOH and toluene, then titrating (electrometrically in 90% acetone and water) to get equivalent weight. Any remaining dodecylamine will show up here as a second break (weaker base) on the titration curve.

6. Near the end the product was very thick and bubbled over into the receiver frequently.

N-(Primene 81R)-N', N''-di(o-tolyl)guanidine. Carbodiimide Method.



20 g (0.1 moles) of Primene 81R was added slowly to 22.4 g (0.1 moles) of di(o-tolyl)carbodiimide, swirled, (the temp. rose to 75°) and clamped in the steam bath with a drying tube for 24 hours. The mixture was cooled, taken up in 400 ml of toluene and stirred as anhydrous HCl was bubbled through. The hydrochloride solution was washed 2 times with 11. of water and evaporated under reduced pressure. Yield:45%.

1,3-di(2-ethylhexyl)thiourea - 258 g (2 moles) of 2-ethylhexylamine were added to 96 g (1.26 moles) of carbon disulfide and 250 ml of water with good stirring. The temp. went to 70°. After two hours, 90 g of 50% NaOH (1.12 moles) was added, causing the thick mixture to become even thicker. The mixture was heated to reflux 3 hrs. It was thin again, and yellow by the time it reached reflux, and orange 30 min. later. After standing overnight, the mixture was acidified with HCl and turned yellow again and was extracted with chloroform. The chloroform solution was washed 3 times with hot water, the 1st wash containing HCl. The chloroform solution was filtered and evaporated in vacuo. Yield: 240 g = 80%.

S-Ethyl-N, N'-di(2-ethylhexyl)thiuronium bromide

80 g (0.27 moles) of 1,3-di(2-ethylhexyl)thiourea and 33 g (0.30 moles of ethyl bromide were mixed in 50 ml of ethanol and heated to 55-60° for 1-1/2 hrs. The solvent and excess ethyl bromide were removed in vacuo to a constant weight.

Yield 99 g = 91%. Analysis C = 57.9 H = 10.6, N = 7.2, Br = 19.1, S = 7.7
Calculated C = 55.8, H = 10.1, N = 6.8, Br = 19.5, S = 7.8.

N-Phenethyl-N', N''-di(2-ethylhexyl)guanidinium bromide

48 g (0.12 moles) of S-ethyl-N, N'-di(2-ethylhexyl)thiuronium bromide were dissolved in 200 ml of ethanol and 71 g (0.59 moles) of phenethyl amine added. The mixture was heated at 60° overnight. An excess of aqueous HBr was added and the mixture boiled to 90° to remove ethanol and ethyl mercaptan. Chloroform was added to the residue,

and the solution washed 3 times with hot water after the original aqueous phase was removed. The chloroform was evaporated under reduced pressure, and the crude product partitioned between 625 ml of 80% ethanol and 300 ml of hexane. The ethanol solution was washed 2 times more with 300 ml of hexane and the ethanol solution evaporated under reduced pressure to a constant weight. KOH equiv. wt. : 498 Calculated eq. wt. : 468.

APPENDIX II

DETERMINATION OF ALKYLAMMONIUM IONS IN AQUEOUS SOLUTION

PICRATE METHOD

Reagents:

1. 2×10^{-3} M picric acid in a pH 3 citrate/phosphate buffer solution*

2. Reagent grade chloroform

Procedure:

1. Pipet 5 ml. each of the picrate reagent and chloroform into a 20 ml vial.

2. Pipet 5 ml. of aqueous sample (approximately neutral) into the reagents. Also prepare a reagent blank using 5 ml. of distilled water instead of the sample.

3. Shake 5 min., centrifuge, and collect the organic phase.

4. Read absorbance at 410 mμ in a 1 cm. cell. The amine concentration is determined from a curve for the particular amine. This is made by shaking chloroform solutions in the range of $0\text{-}5 \times 10^{-5}$ M amidine with the buffered picrate solution and reading the absorbance of the organic phase. Blanks should typically be less than 0.02.

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* 458 mg picric acid, 16.7 g. citric acid monohydrate, and 5.84 g. anhydrous disodium phosphate in 1 liter of water. Solution is 0.079 M in citrate, and 0.041 M in phosphate.

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APPENDIX III

pKa of Amidines

Table III-1 Apparent pKa of Amidines in 0.010 M NaCl

	Concentrations, M			
Compound	$(\bar{B})$	$(\overline{BHX})$	pH	pKa
in toluene				
Cy2 NoA	0.051	0.285	7.95	9.54
	0.077	0.055	8.08	9.78
	0.102	0.0785	8.20	9.92
	0.153	0.128	8.40	10.14
	0.255	0.229	9.00	10.55
Eh_2EhA	0.0503	0.049	6.42	8.40
	0.0754	0.074	6.70	8.68
	0.1005	0.100	6.76	8.75
	0.1508	0.150	7.02	9.01
	0.2513	0.250	7.13	9.12
in Chevron 3				
Eh_2EhA	0.0514	0.049	6.42	8.40
	0.0776	0.074	6.57	8.53
	0.103	0.100	6.71	8.68
	0.153	0.152	6.90	8.88
	0.256	0.255	7.10	9.08
	0.446	0.050	7.60	8.65
	0.371	0.125	7.35	8.86
	0.256	0.255	7.10	9.08
	0.121	0.375	6.95	9.44
	0.046	0.450	6.70	9.69
Eh_2OcA	0.051	0.051	7.27	9.26
	0.076	0.766	7.30	9.29
	0.103	0.102	7.47	9.46
	0.154	0.153	7.57	9.56
	0.257	0.255	7.82	9.81
EhOcEhA	0.045	0.051	6.94	8.99
	0.067	0.0766	6.92	8.70
	0.090	0.102	7.14	9.18
	0.134	0.153	7.22	9.27
	0.224	0.255	7.54	9.59

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APPENDIX III

Table III-1 (Cont'd)

	Concentrations, M			
Compound	$(\bar{B})$	$\overline{(BHX)}$	pH	pKa
DoEhEhA				
	0.098	0.102	6.81	8.83
	0.146	0.153	7.09	9.11
	0.244	0.255	7.40	9.42
	0.436	0.048	7.68	8.62
	0.351	0.133	7.49	9.06
	0.244	0.255	7.40	9.42
	0.118	0.366	7.00	9.49
	0.046	0.438	6.44	9.41
	0.780	0.084	7.90	8.92
	0.647	0.212	7.85	9.37
	0.430	0.434	7.70	9.69
	0.212	0.652	7.23	9.70
	0.084	0.780	6.82	8.77
DoEhNdA	0.052	0.052	5.45	7.45
	0.078	0.078	5.80	7.80
	0.104	0.104	5.75	7.75
	0.155	0.156	5.50	7.50
	0.260	0.259	6.25	8.25

TABLE III-2

pKa OF ALIPHATIC AMINES IN 0.010 M NaCl

Compound	Concentrations, M			
	(B)	(BHCl)	pH	pKa
Primene JM-T	1.17	0.12	6.50	7.51
	0.89	0.30	6.30	7.83
	0.60	0.60	6.00	8.00
	0.30	0.89	5.69	8.16
	0.12	1.17	5.00	7.99
Amberlite LA-2	0.91	0.21	4.85	6.21
	0.70	0.42	4.6	6.4
	0.49	0.63	4.3	6.4
	0.28	0.84	3.9	6.4
	0.06	1.06	3.2	6.4

TABLE III-3

APPARENT pKa OF Eh_2EhA/CHEVRON 3 IN NITRATE SYSTEMS

		Concentrations, M					
Compound	$(\bar{B})$	$(\overline{BHX})$	pH	pKa	(NH_3)	(NH_4^+)	(NO_3^-)
Aqueous: 0.010 M Sodium Nitrate							
	0.097	0.101	8.25	10.26			
	0.145	0.150	8.45	10.46			
	0.242	0.252	8.74	10.76			
Aqueous: 1.0 M (NH_3 + NH_4NO_3); Organic 0.50 M Amidine							
	0.78	0.42	9.42	10.4	.45	.54	0.54
	0.22	0.28	9.72	10.3	.62	.36	0.36
	0.48	0.017	9.96	9.1	.75	.24	0.24

APPENDIX IV

SOLUBLE LOSS OF AMIDINE HYDROCHLORIDES

Organic diluent, Chevron 3, except as noted; aqueous phase, sodium chloride

Compound	Concentrations, M			K_s
	$\overline{(BHCl)}$	(Cl^-)	(BH^+)	
$Cy_2NoA \cdot HCl$ (toluene)				
	0.083	0.015	5.2×10^{-3}	1060
	0.087	0.033	3.0×10^{-3}	880
	0.091	0.101	8.0×10^{-3}	1130
	0.092	0.300	2.8×10^{-4}	1090
$Eh_2EhA \cdot HCl$ (toluene)				
	0.1013	0.0102	1.8×10^{-4}	5.5×10^{4}
	0.1014	0.0301	8.5×10^{-5}	4.0×10^{4}
	0.1015	0.10	3.1×10^{-5}	3.3×10^{4}
	0.1015	0.30	1.8×10^{-5}	1.7×10^{4}
$Eh_2OcA \cdot HCl$				
	0.100	0.0102	1.5×10^{-4}	6.5×10^{4}
	0.100	0.0301	5.7×10^{-5}	5.3×10^{4}
	0.100	0.100	3.5×10^{-5}	2.9×10^{4}
	0.100	0.300	3.5×10^{-5}	9.5×10^{3}
$EhOcEhA \cdot HCl$				
	0.096	0.0102	2.2×10^{-4}	4.3×10^{4}
	0.096	0.0301	1.16×10^{-4}	2.75×10^{4}
	0.096	0.100	5.3×10^{-5}	1.8×10^{4}
	0.096	0.300	2.1×10^{-5}	1.5×10^{4}
$Eh_2EhA \cdot HCl$				
	0.100	0.0105	4.9×10^{-4}	1.94×10^{4}
	0.101	0.0302	1.92×10^{-4}	1.74×10^{3}
	0.101	0.101	6.75×10^{-5}	1.48×10^{3}
	0.101	0.300	4.25×10^{-5}	7.92×10^{3}
	0.20	0.01	5.3×10^{-4}	3.8×10^{4}
	0.60	0.01	6.6×10^{-4}	9.1×10^{4}
	1.00	0.01	8.8×10^{-4}	11.4×10^{4}
$DoEhNdA \cdot HCl$				
	0.104	0.010	2.8×10^{-5}	3.7×10^{5}
	0.104	0.030	4.6×10^{-5}	7.5×10^{4}
	0.104	0.10	1.3×10^{-5}	8.0×10^{4}
	0.104	0.30	1.0×10^{-5}	3.5×10^{4}
$DoEhEhA \cdot HCl$				
	0.098	0.010	8×10^{-6}	1.2×10^{6}
	0.098	0.010	13×10^{-6}	0.75×10^{6}
	0.098	0.010	3×10^{-6}	3.3×10^{6}

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6 *Title*

Nitrate Removal from Waste Waters by Ion Exchange

10 *Author(s)* Grinstead, Robert R. Jones, Kenneth C.	16 *Project Designation* Project #17010, Contract #14-12-808 21 *Note*

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23 *Descriptors (Starred First)*

*Nitrates, *Denitrification, *Anion Exchange, Waste Water Treatment, Municipal Wastes, Water Pollution Treatment, Resins, Tertiary Treatment, Solvent Extractions.

25 *Identifiers (Starred First)*

Amidines

27 *Abstract*

This report described an exploratory experimental study of the use of porous polymer beads containing a water-immiscible extractant system for the removal of nitrate from waste waters. Alkylated amidines proved to be a suitable class of compounds for the extractant system. They are relatively strong bases, and exist in the salt form in contact with waste waters in the pH range of 7-8. They can, however, be readily regenerated with alkalis, such as ammonia or sodium hydroxide.

The amidinium ion in the organic phase selectively extracts nitrate ion over chloride ion by a factor of about 20 (i.e., the nitrate/chloride ratio in the organic phase is about 20 times the ratio in the equilibrium aqueous phase), and nitrate over sulfate and bicarbonate by much higher ratios. From typical municipal waste waters amidine systems will therefore pick up mainly the nitrate ion.

Amidines dissolved in an aromatic hydrocarbon were absorbed in macroporous polystyrene beads and used to treat a synthetic municipal waste water containing 62 ppm nitrate ion and 350 ppm chloride ion. Beds of this material treated up to 70 bed volumes of water prior to breakthrough of the nitrate in the effluent. The absorbed nitrate ion was removed with either ammonia or sodium hydroxide.

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